

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

**2014 DOE Hydrogen and Fuel Cell Program Review**

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**Northeastern University, 360 Huntington Av., Boston, MA 02115**



**June 17<sup>th</sup>, 2014**

Project ID# FC086

# Overview



## ➤ Timeline:

- Project Start date: 8/01/2010
- Project End date: 5/31/2015
- Percent complete: 75% (12 months remaining)

## ➤ Budget Data:

- Total Funding Spent as of 3/31/2014: \$4,328,090
- Total Project Value: \$6,380,015 = \$4,942,301 (DOE) + \$1,437,714 (cost share 22.5%)

## ➤ Barriers/Targets

- Activity Targets for Non-PGM Catalysts
  - Budget Period 1: **Volumetric Activity:** to exceed 300 A/cm<sup>3</sup> (2015 target) and **Areal Activity:** 100 mA/cm<sup>2</sup> at 0.8 V 1.5 bar total pressure.
  - Budget Period 2: **Areal Activity (Air):** 30 mA/cm<sup>2</sup> at 0.8 V (Q2, FY14) and 1.0 A/cm<sup>2</sup> at 0.4 V (Q5, FY15) in H<sub>2</sub>/Air, 2.5 bar total pressure.
  - **Durability at Temperatures ≤ 80°C:** 2000 hrs (2010); 5000 hrs (2015)

## ➤ Partners

- Northeastern Univ., (Prime) Boston: S. Mukerjee (P.I)
- Univ. of New Mexico, Albuquerque: Prof. P. Atanassov
- Michigan State University: Prof. S. C. Barton
- Pajarito Powders, Albuquerque, NM, Dr. B. Halevi
- Nissan Technical Center North America (NTCNA): Dr. N. Dale
- 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 targets for activity and durability. The 2015 activity targets for this project are 100 mA/cm<sup>2</sup> (H<sub>2</sub>/O<sub>2</sub>, 1.5 bar total pressure) and 30 mA/cm<sup>2</sup> @ 0.8 V and 1 A/cm<sup>2</sup> at 0.4 V (H<sub>2</sub>/Air) at 2.5 bar total pressure .
- 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 tolerance to poisons which typically effect Pt & Pt alloys (i.e., sulfur, CO etc.), Hence ability to tolerate H<sub>2</sub> with greater impurity.

# Overall Approach

## Overall Technical Approach:

- **Comprehensive materials development strategy encompassing**
  - **Novel new reaction Centers for Oxygen Reduction**
    - High Performance Catalysts
    - Tailored Catalysts for Understanding Structure Property Relationships
  - **Controlling Metal support interactions**
    - 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
- **Ex Situ XPS and In Situ 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 ~ 150 A/cm<sup>3</sup> which is close to 2010 DOE target. The 2015 target is 300 A/cm<sup>3</sup> which requires the following approach to materials development**
  - (a) Development of new classes of materials,
  - (b) Redesign of the catalyst support and electrode structure for efficient mass transport
  - (c) Understanding ORR electrocatalysis using a combination of spectroscopy and computation
  - (d) Determining degradation pathways under actual operando conditions.

***Our approach addresses all these issues for meeting 2015 DOE targets.***

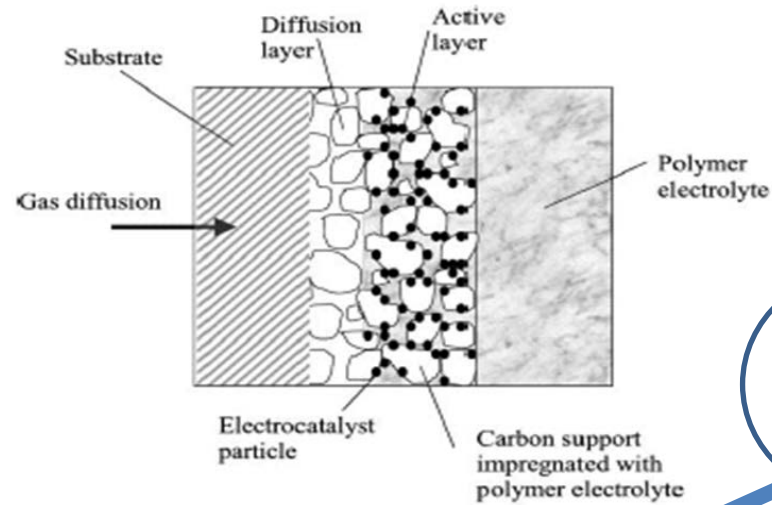
# Quarterly Milestones

- **Q1 (3/31/14 due date):** First batch of the scaled up non-PGM catalyst samples (at least 30 g) tested for kinetic reproducibility both intra and inter sample basis with variation of the activity, as measured by RDE, being  $\leq \pm 5\%$ .

*Status: As shown below, the project Objectives have been met.*

- **Q2 (6/30/14 due date):** Finish both the intra and inter sample analysis of fuel cell data (MEA single cell performance) measured at Nissan Technical Center scheduled for March 2014, confirming a) performance obtained in other laboratories or b) trends identified in other laboratories.
- **Q3 (9/30/14 due date):** Using non-PGM cathode catalysts, demonstrate MEA performance of at least 30 mA/cm<sup>2</sup> at 0.8 V in H<sub>2</sub>/Air, 2.5 bar total pressure.
- **Q4 (12/31/14 due date):** Non-PGM catalysts subjected to catalyst stability (<10% loss of initial activity loss) and load cycle testing will achieve a loss of initial catalytic activity of < 60% and less than 30 mV loss in potential at 0.8 A/cm<sup>2</sup>.
- **Q4 (12/31/14 due date):** Demonstrate a unified mechanism for ORR wherein the active site and its function are identified for a range of Non-PGM catalysts prepared with different approaches leading to a better fundamental understanding of the requirements for a non-PGM ORR catalyst. A detailed report will be submitted or accepted in a peer reviewed journal.
- **Q5 (3/31/15 due date):** With a cathode optimized for non-PGM catalysts, achieve MEA performance of at least 1.0 A/cm<sup>2</sup> at 0.4 V in H<sub>2</sub>/Air, 2.5 bar total pressure.

# Program Structure and Management



Nano-Engineering of Reaction Centers for Non-PGM Interfaces  
**Thrust Area 1 - Task 1.1-1.2**

Metal Inorganic Framework Structures [NEU]

Open Framework Structures [UNM]

Non Metal Polymer Complexes [MSU, NEU, UNM]

Bio-Inspired Non PGM Transition Complexes [NEU]

Designing Interfacial Structures for Enhanced Mass Transport (NEU, MSU)  
**Thrust Area 2 – Task 2.1**

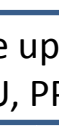
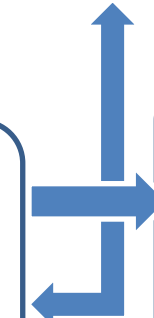
Computation (MSU) and Spectroscopy XPS (UNM) and in situ Synchrotron Spectroscopy (NEU)  
**Thrust Area 4 - Task 3.1-3.3**

MEA Fabrication, Initial Validation and Single Cell Testing  
**Thrust Area 3 - Task 2.2**

Electrocatalyst Scale up (PPC) and MEA Fabrication (NEU, PPC) **Task 1.3**

Single Cell Validation Tests and Durability Protocol Implementation (NTCNA /LANL)  
**Thrust Area 5 - Task 2.3**

Automotive Test Protocols, Stack Testing and Durability Validation (NTCNA)  
**Thrust Area 5 - Task 2.4**

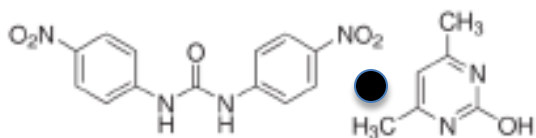


# Task 1.1-1.2: Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

## Advanced Performance Catalysts: Development of Novel MNC Catalysts

### Materials Design Strategy: Evolution of Different Approaches in Budget Period 1... Continued

#### ❖ Mechano-Chemical Approach (UNM)



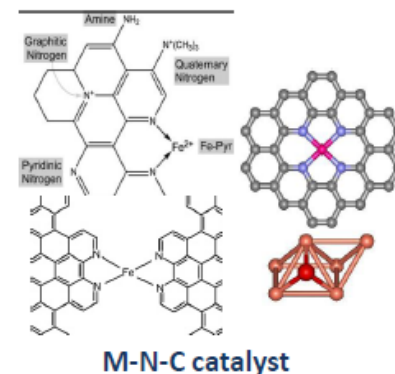
Nicarbazine

+ Fe-Salt+ Silica templated

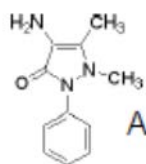
UNM-CTS

Ball milling

Pyrolysis



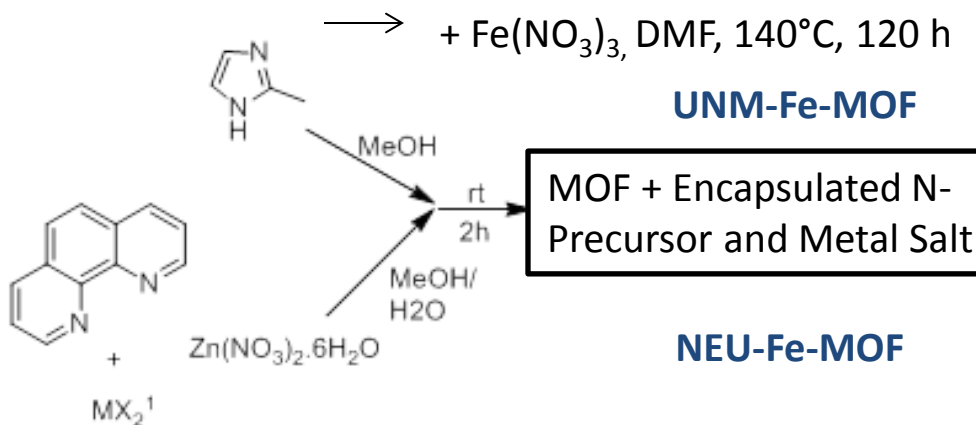
#### ❖ N-Chelating Precursor-Metal Salt Approach (UNM, MSU)



Aminoantipyrine

+ Fe-Salt+ Silica templated

#### ❖ Metal Organic Framework Approach: (NEU)

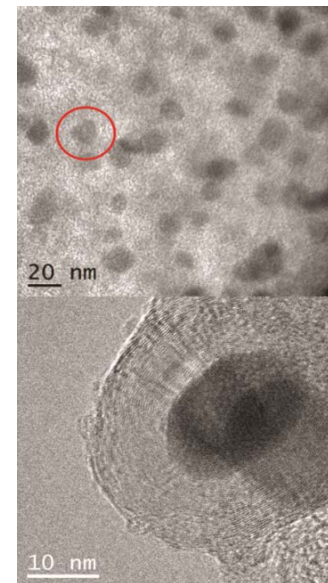
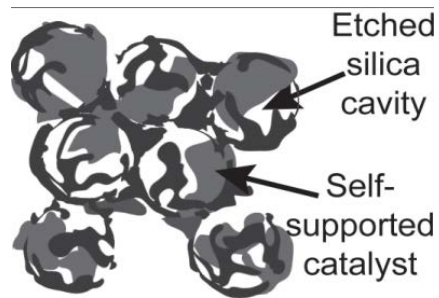
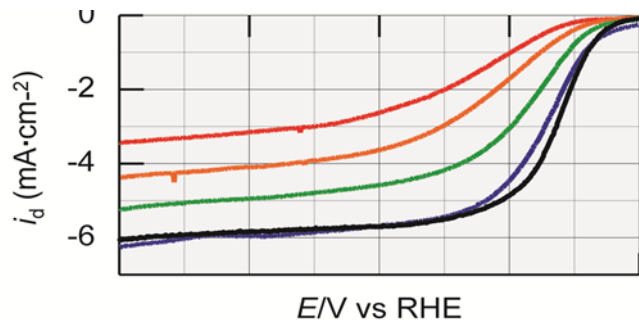
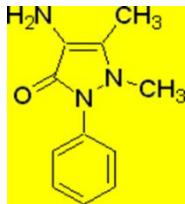


[1] M=Fe, Co; X=C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, Cl

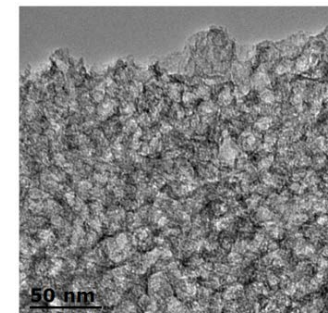
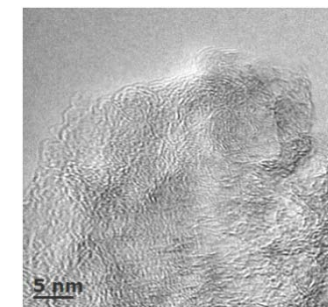
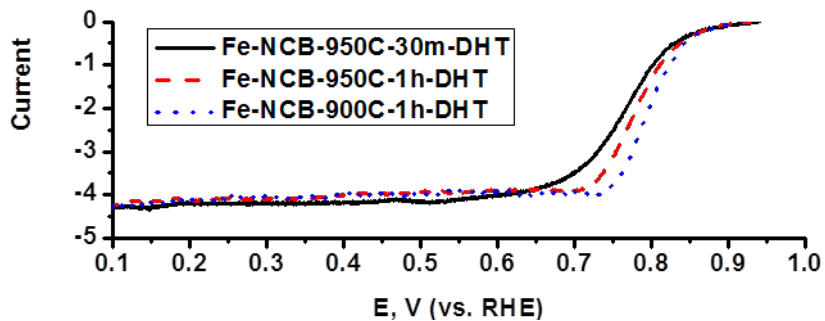
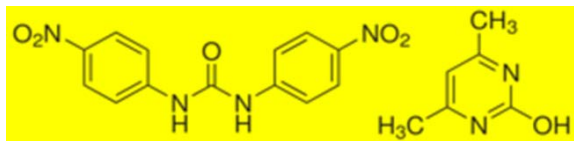
[2] '@' indicates chemical encapsulation of phenanthroline and metal (M-N<sub>4</sub> active site)

# University of New Mexico Catalysts

## Aminoantipyridine derived catalyst: (Fe-AAPyr)



## Fe-Nicarbazim-Fe-NCB: Charge Transfer Salt (CTS)



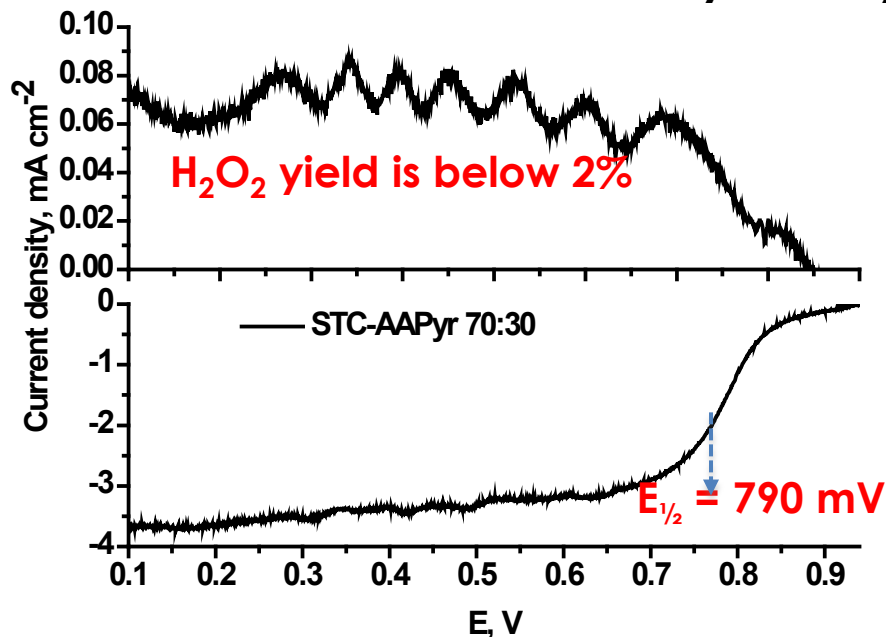


# Fe-Nicarbazim/Fe-AAPyr Blend



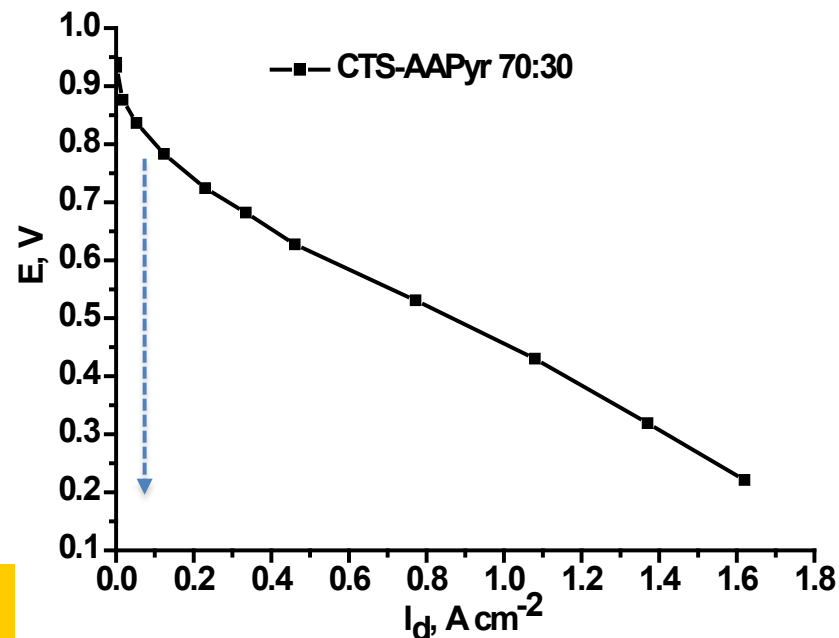
THE UNIVERSITY of  
NEW MEXICO

RRDE and MEA data on STC-AAPyr catalyst



Catalyst Loading is 0.6 mg/cm<sup>2</sup>  
O<sub>2</sub>, 0.5 H<sub>2</sub>SO<sub>4</sub>, 1200 RPM, 5mV/s, RHE

Meets and exceeds current target of 0.1 A @ 0.8V with NO iR correction



DOE recommended: 100% RH,  
H<sub>2</sub>/O<sub>2</sub>, T<sub>cell</sub> = 80°C, 0.5 bar<sub>g</sub>

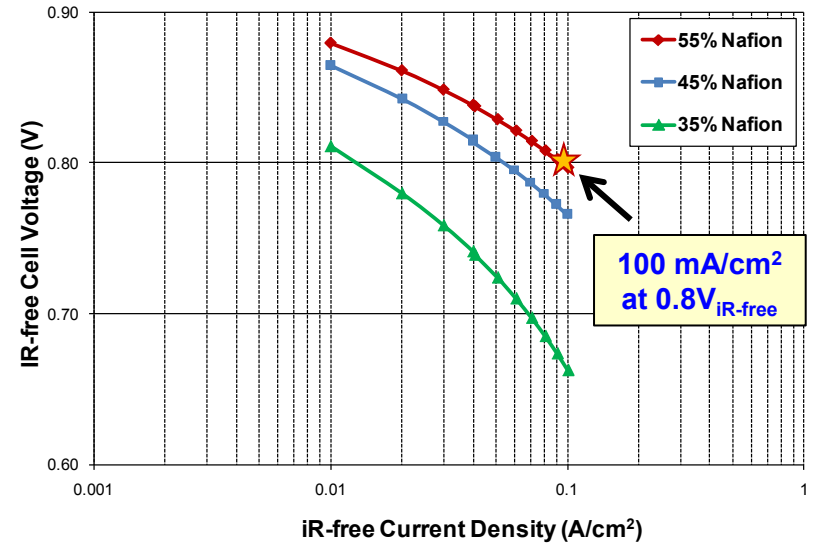
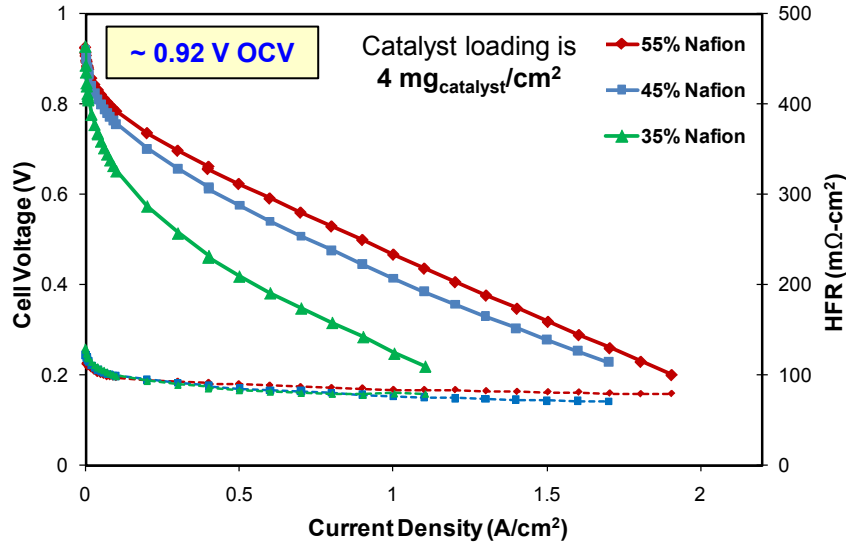
A. Serov, B. Halevi, K. Artyushkova, P. Atanassov, Non-PGM Cathode Catalysts for Fuel Cell Application Derived from Heat Treated Heteroaromatic Amine Precursors, *US Patent Appli. 12/42609*, June 15, 2012, PCT/US12/42609

A. Serov, P. Atanassov, Non-PGM Catalysts for ORR Based on Charge Transfer Organic Complexes *Provisional Application 61/753,123* filed on January 16, 2013, PCT filed on January 13, 2014

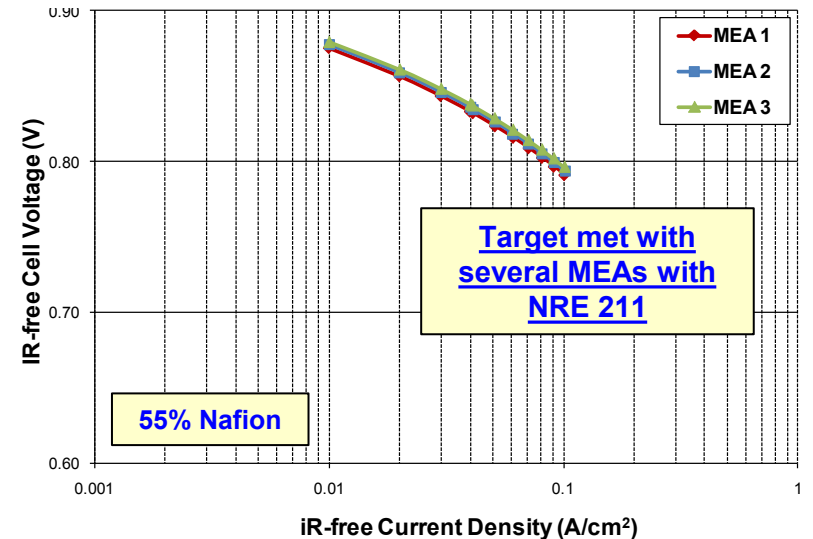
# Milestone- DOE Go/No Go Decision

## Task 2. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR) MEA Validation Test Performed at NTCNA on UNM CTS Catalysts

**H<sub>2</sub>/O<sub>2</sub> 80 °C 100% RH 1.5 bar Total Pressure (DOE standard conditions, 1.0 bar<sub>g</sub>)**



- ❑ Increasing the Nafion® content while keeping the catalyst loading constant at 4 mg/cm<sup>2</sup> significantly affects the iV performance.
- ❑ The UNM CTS non-PGM catalyst with 55% Nafion showed very good iV performance, giving 100 mA/cm<sup>2</sup> at 0.8V<sub>IR-free</sub>.
- ❑ These results have been reproduced using three MEAs from different catalyst batches.



# Milestone - DOE Go/No Go Decision

## DURABILITY- Fuel Cell Data Validation by NTCNA

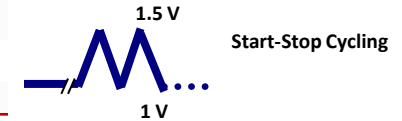
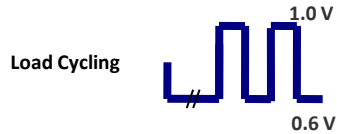


The stability of Fe-CTS was evaluated under Nissan load cycling and start-stop cycling protocols

### Protocols for Nissan and DOE Durability Working Group

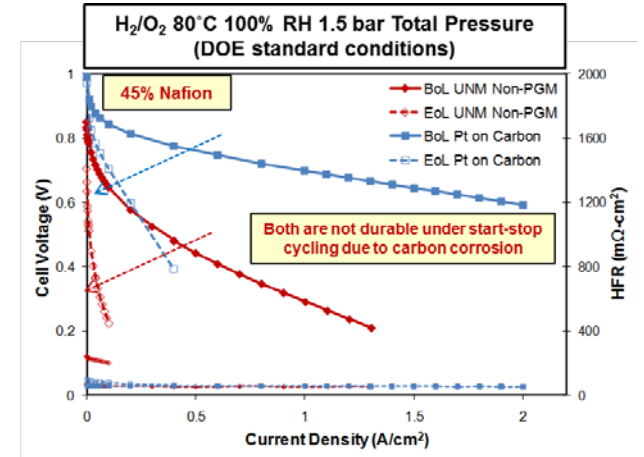
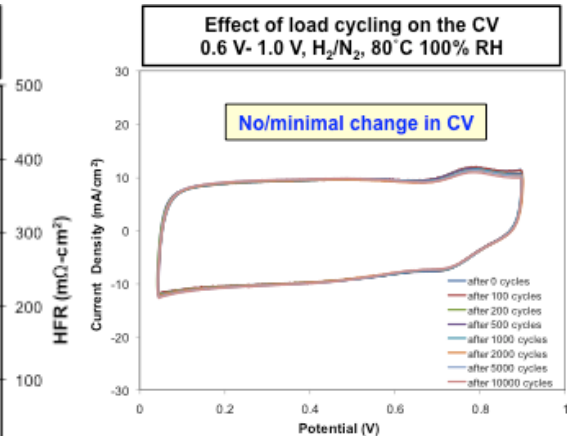
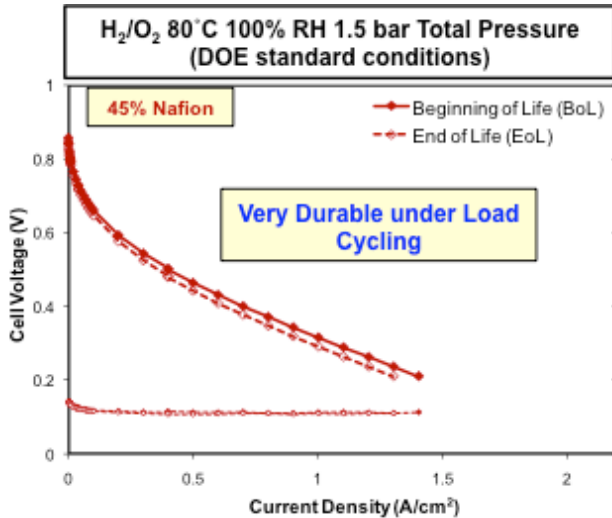
Condition	Nissan Load Cycling	Nissan Start-Stop Cycling
Temperature (°C)	80	80
Gas condition Cathode	N <sub>2</sub>	N <sub>2</sub>
Gas – Anode	H <sub>2</sub>	H <sub>2</sub>
Voltage scan (V)	[0.6, 1.0]	[1.0, 1.5]
Scan rate (mV/s)	6s/cycle	500
Catalyst loading (mg/cm <sup>2</sup> )		0.6
No. of cycles	10,000	1,000

Nissan evaluates catalyst durability using two protocols: load cycling and start-stop cycling to simulate FC stack conditions.



### Load Cycling

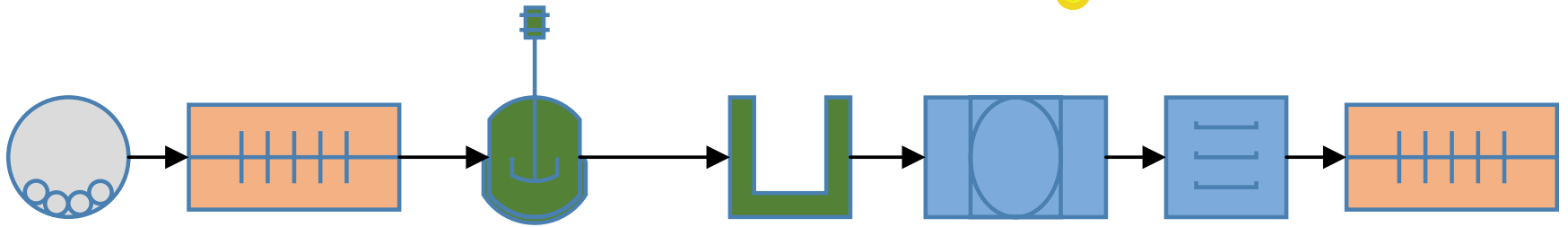
### Start-Stop Cycling



- Minimal change in performance is observed after 10,000 potential cycles (load cycling) from 0.6 to 1.0V. The same durability is observed for 35% and 55% Nafion loading.
- The CV profile barely changed after 10,000 potential cycles. This is also observed for the 35% and 55% Nafion loading MEAs.

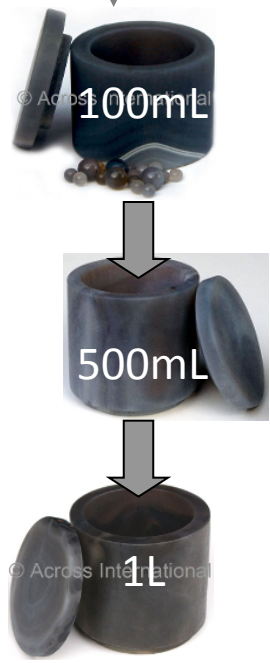
- A similar severe drop in performance is observed for UNM Fe-CTS and traditional Pt on high surface area carbon catalysts.

# Process Diagram and Scale Up



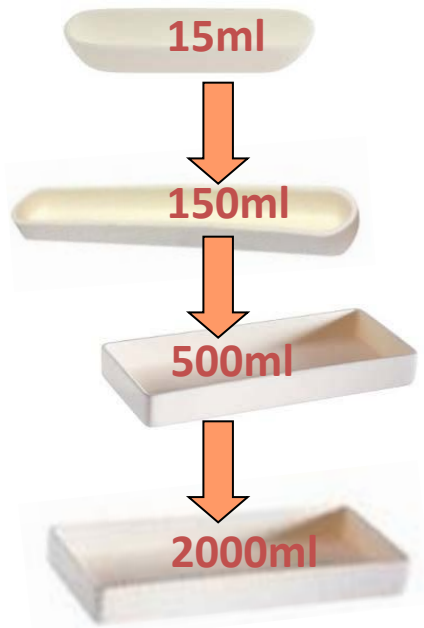
Ball-Mill    Pyrolysis    Etching    Centrifuge    Filter    Dry    Pyrolysis

Scale per batch  
0.5 gr

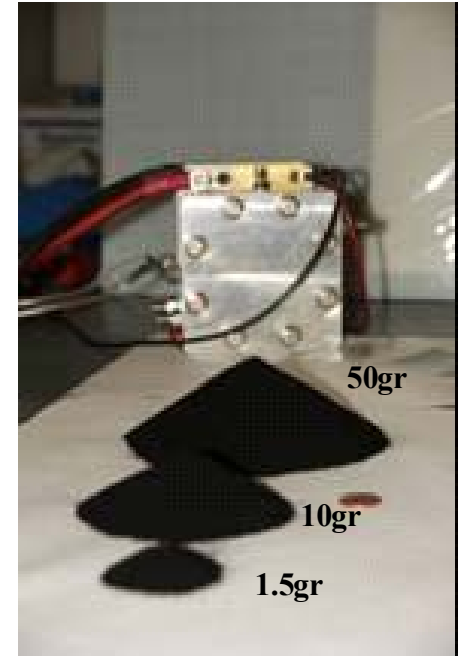
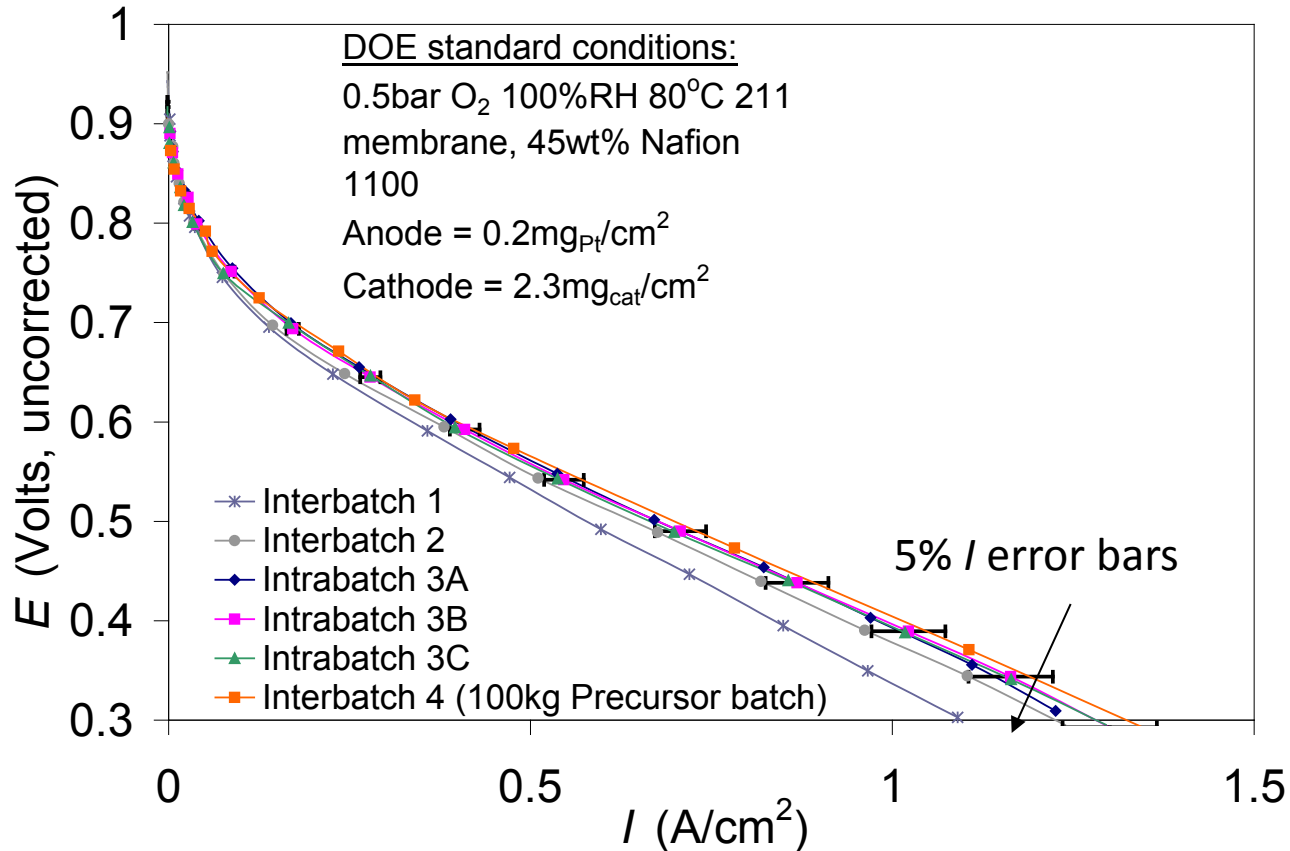


50 gr

100 gr

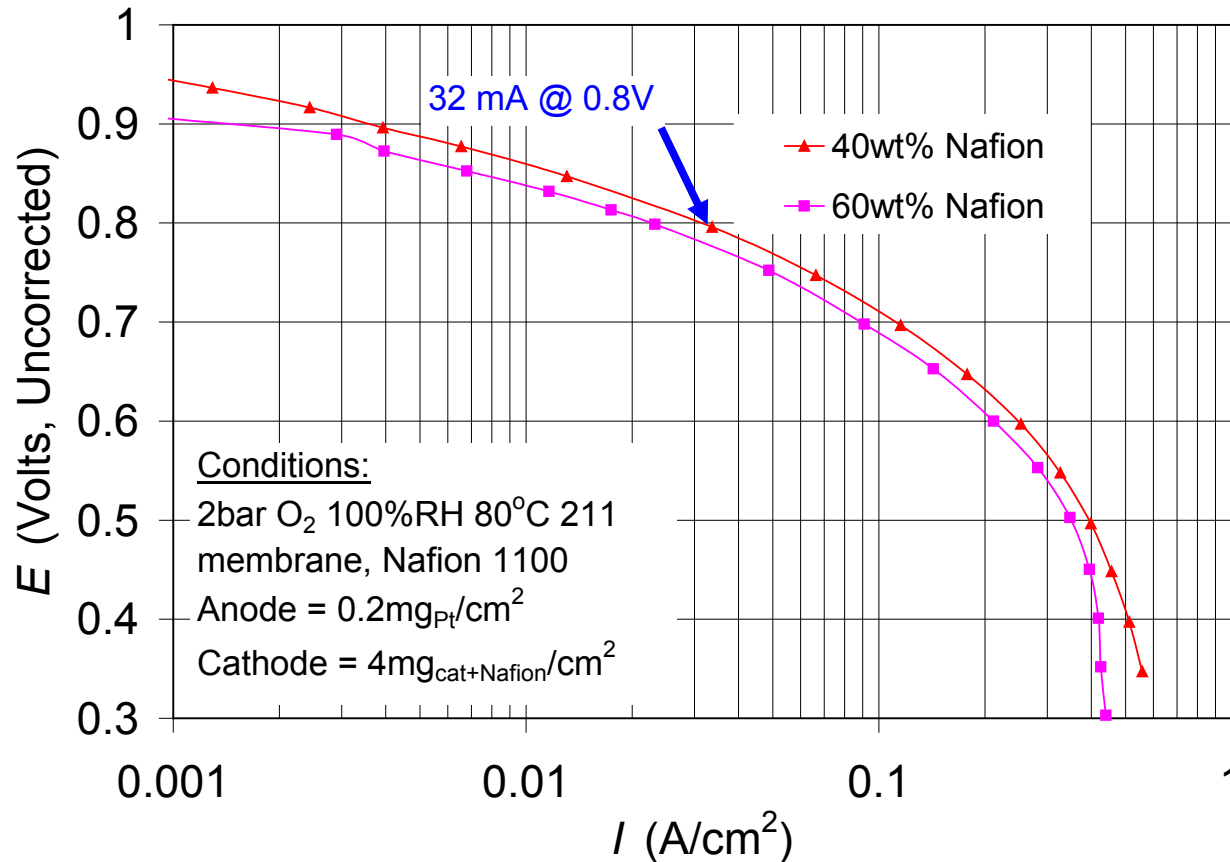


# Fe-CTS scaled up to 50 grams



- ❑ Improvement in performance of 50 gram batches
- ❑ Improved inter-batch variability illustrated by samples 1, 2, 3 and 4
- ❑ Improved intra-batch variability illustrated by performance of 3 GDE made from Sample 3- <5% variability of current at 0.4V
- ❑ Improved performance for different sources of precursors, see batch 4

# Scaled Fe-CTS Performance in Air

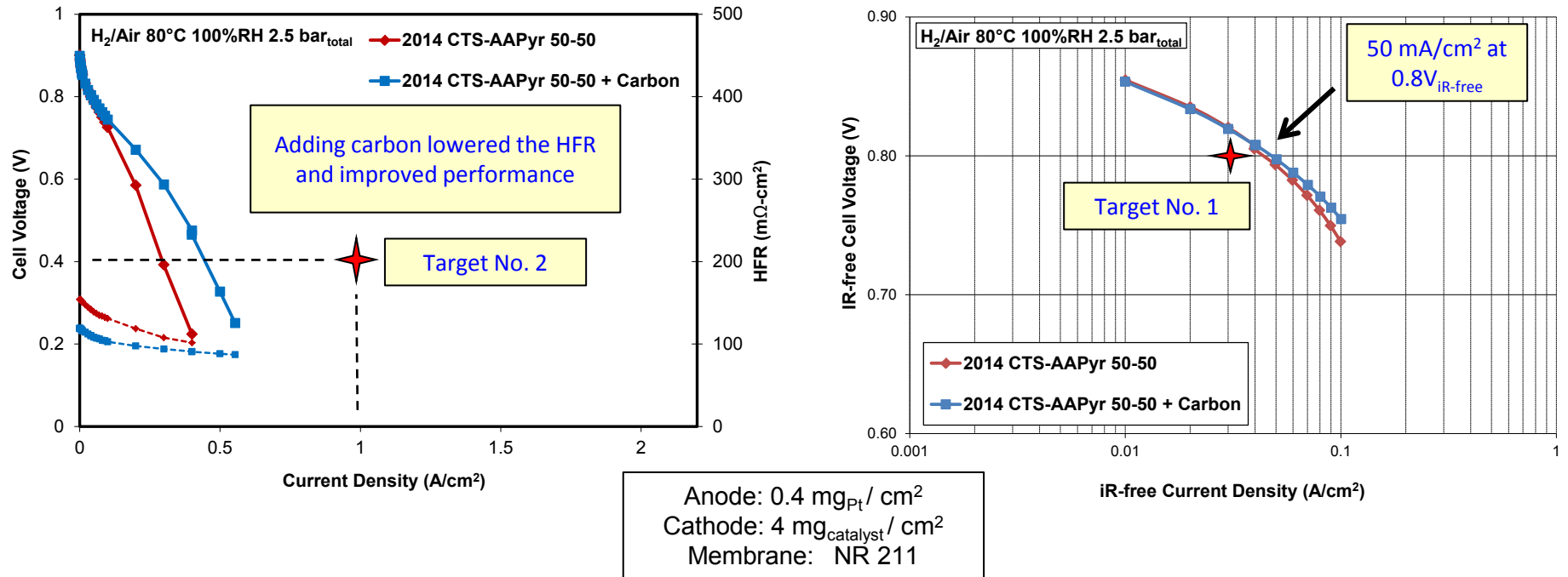


- **40wt% Nafion GDE made from 50-gram batch (Batch 3 in previous slide) achieves 32mA/cm<sup>2</sup> at 0.8V (uncorrected)**

# UNM CTS-AAPyr Catalyst – MEA Testing

## Results – iV Performance: Air

$H_2/Air$  80°C 100% RH 2.5 bar Total Pressure (Project specified standard conditions)



- ❑ The 2014 CTS-AAPyr 50:50 catalyst, with the addition of carbon, exceeded the performance target under Air, giving 50 mA/cm<sup>2</sup> at 0.8V<sub>IR-free</sub>.
- ❑ However, the MEA was not able to achieve the high current density performance target of 0.4 V at 1 A/cm<sup>2</sup>.

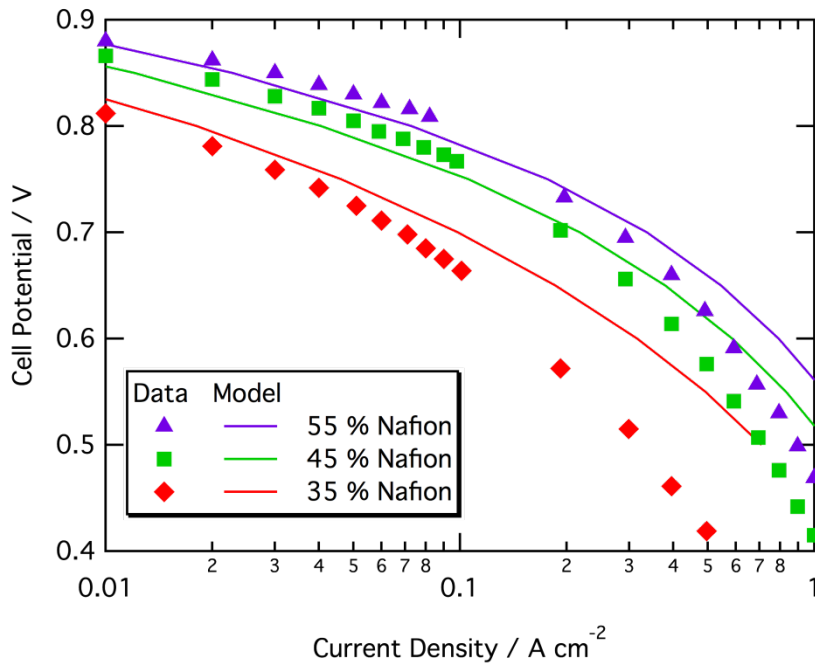
# Model Validation

Experimental data provided by **NISSAN** for catalysts provided by **UNM**

Anode:  $0.4 \text{ mg}_{\text{Pt}}/\text{cm}^2$ , Cathode:  $3.5 \text{ mg}/\text{cm}^2$ , Membrane: NR 211

## Effect of Nafion Content

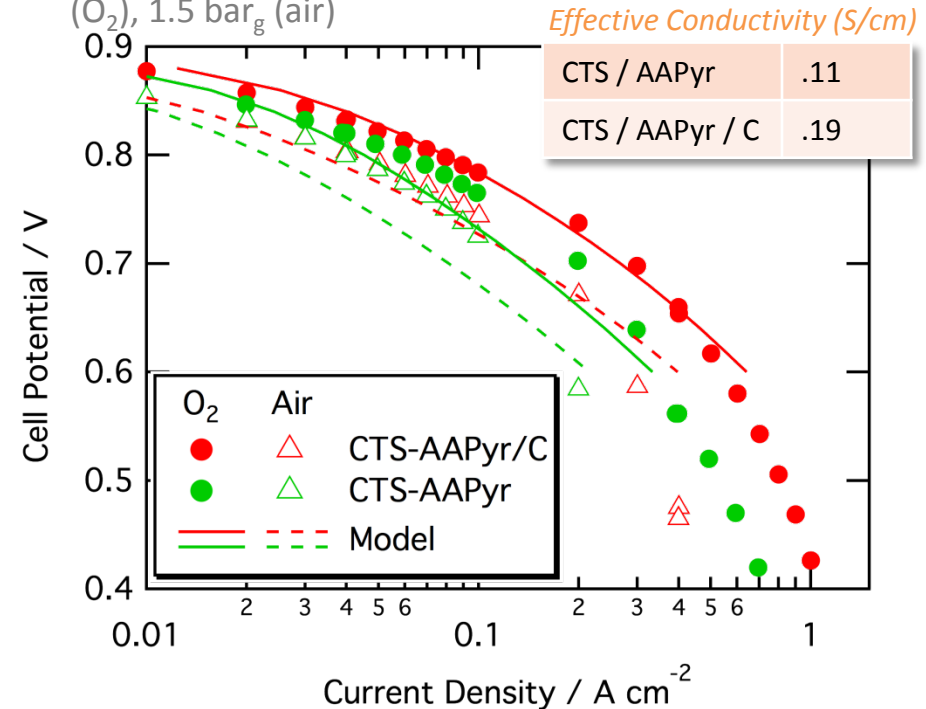
UNM CTS + 25wt% C,  $\text{H}_2/\text{O}_2$   $80^\circ\text{C}$  100% RH,  $0.5 \text{ bar}_g$



- Increased Nafion content increases catalyst **utilization** and ionic **conductivity**
- Model has not fully captured Nafion's impact on water transport.

## Effect of Air

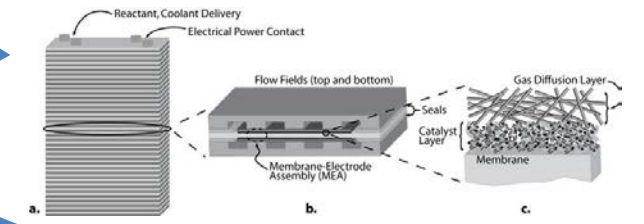
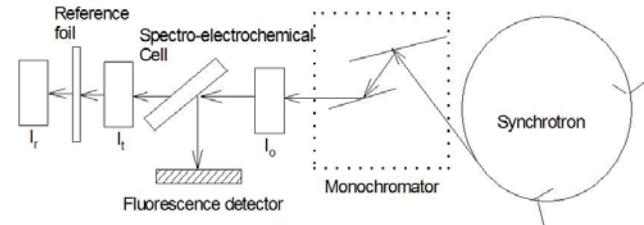
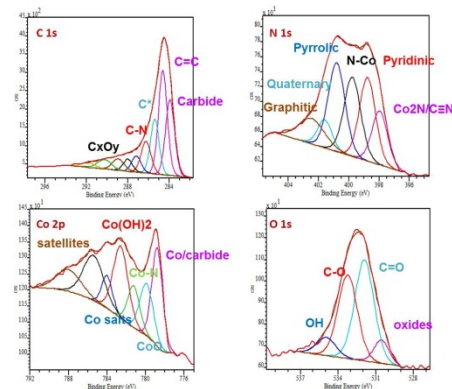
UNM CTS-AAPyr,  $\text{H}_2$ @anode  $80^\circ\text{C}$  100% RH,  $0.5 \text{ bar}_g$  ( $\text{O}_2$ ),  $1.5 \text{ bar}_g$  (air)



- Carbon increases conductivity, and also impacts **porosity** and **hydrophobicity**



# Mechanistic Studies and Spectroscopy



## Participating Institutions:

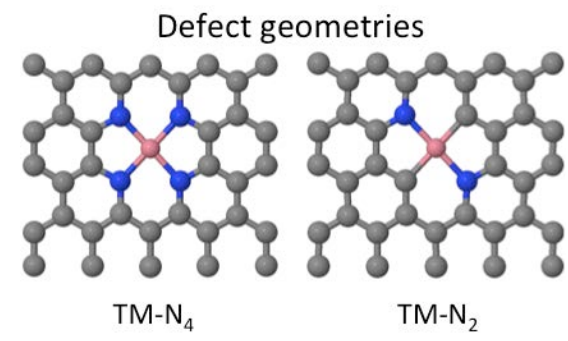
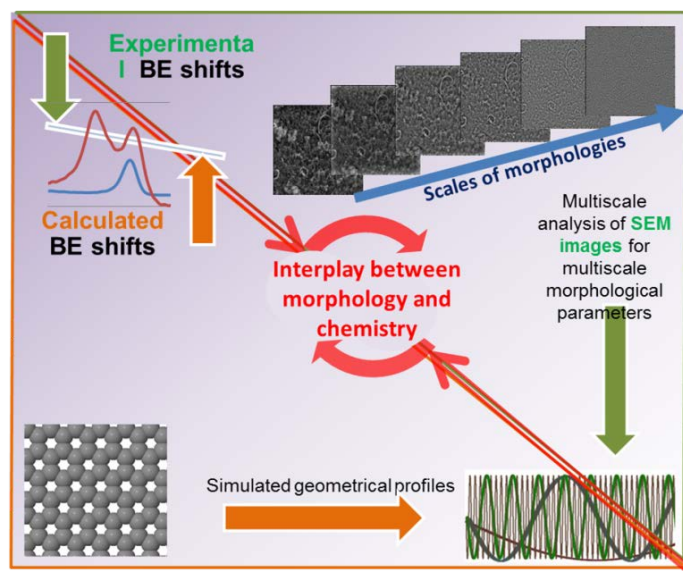
UNM - DFT Calculations

NEU - In situ Spectroscopy with Synchrotron and Raman Measurements

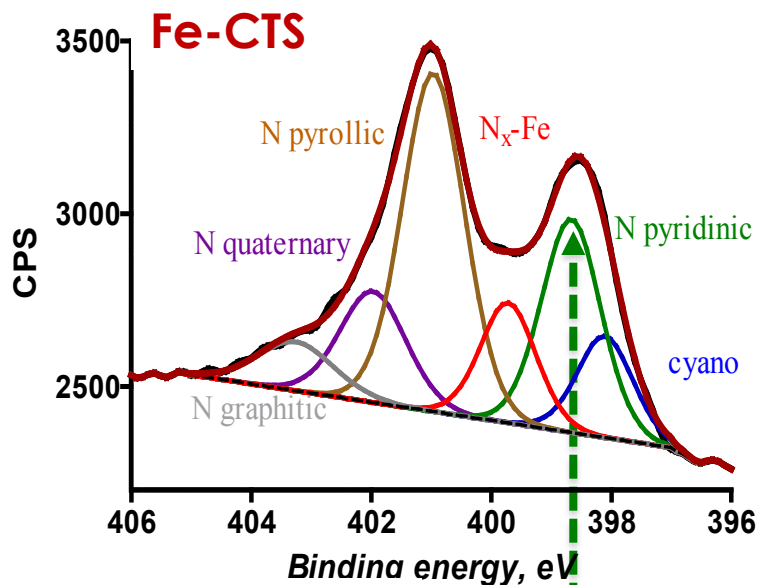
MSU - Macroscopic Modeling

MSU - Molecular Level Computation (Ab-Initio and DFT)

UNM- DFT calculations with XPS and PCA analysis

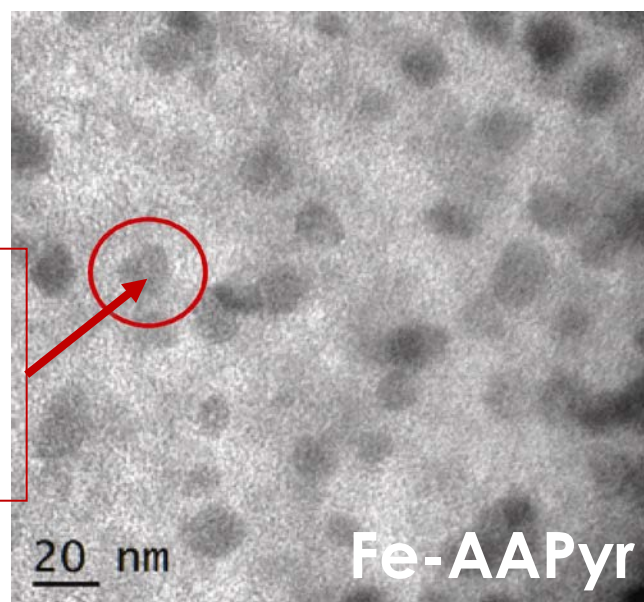
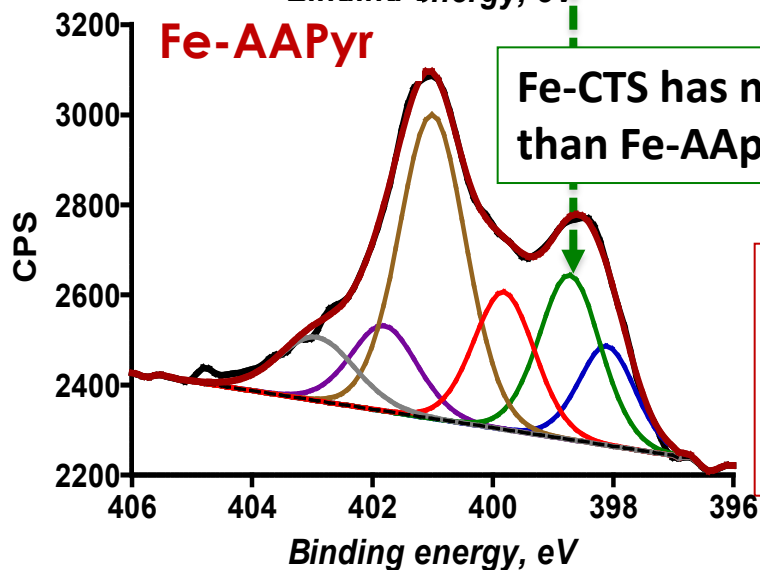
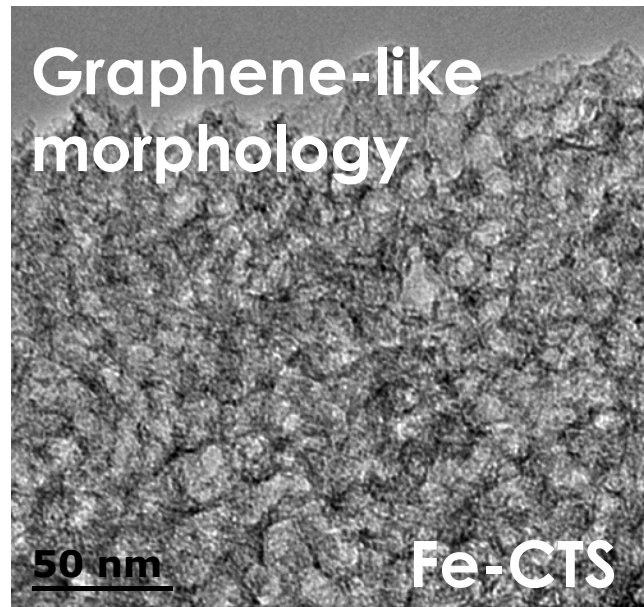


# Two Catalysts: Fe-CTS and Fe-AApyr

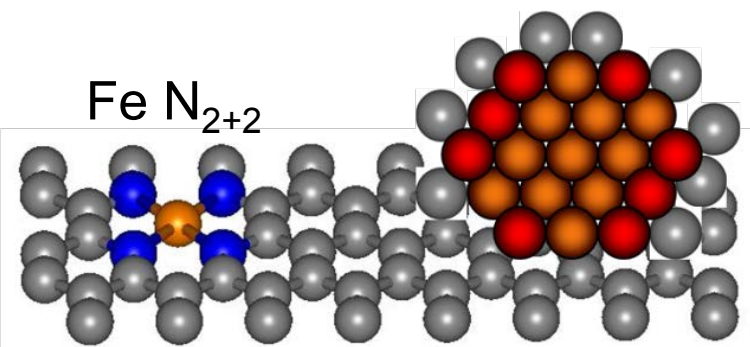


Both catalysts have very similar overall surface composition as evidenced by XPS

Fe-CTS displays more uniform morphology.

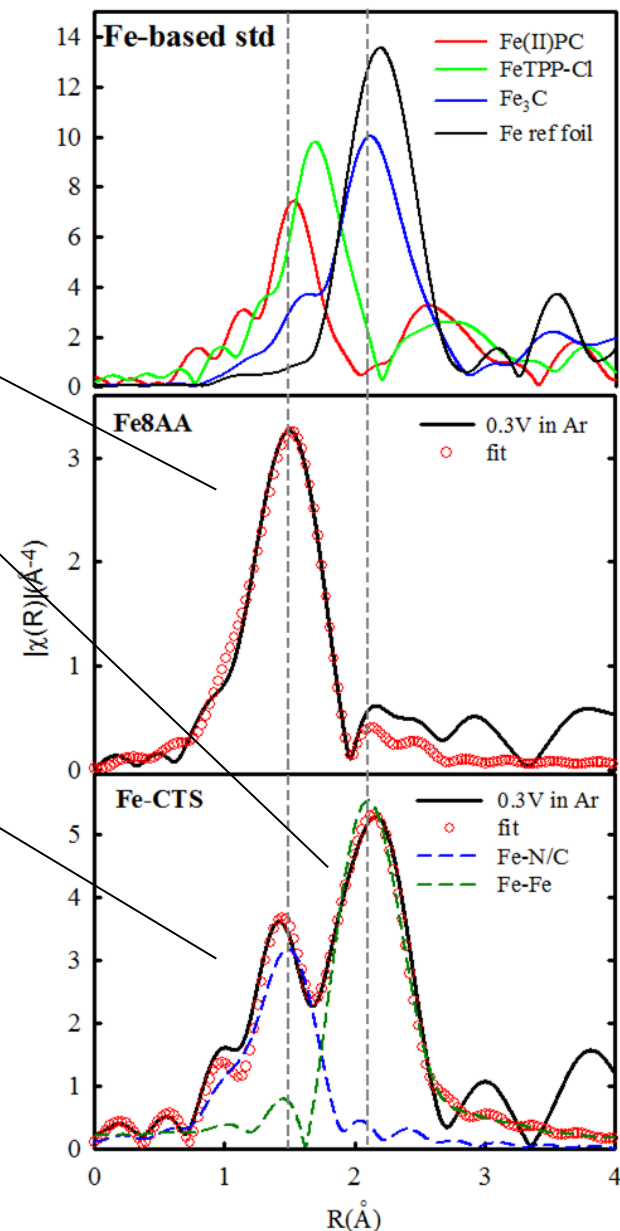


# Basic Structure of Non PGM Catalysts

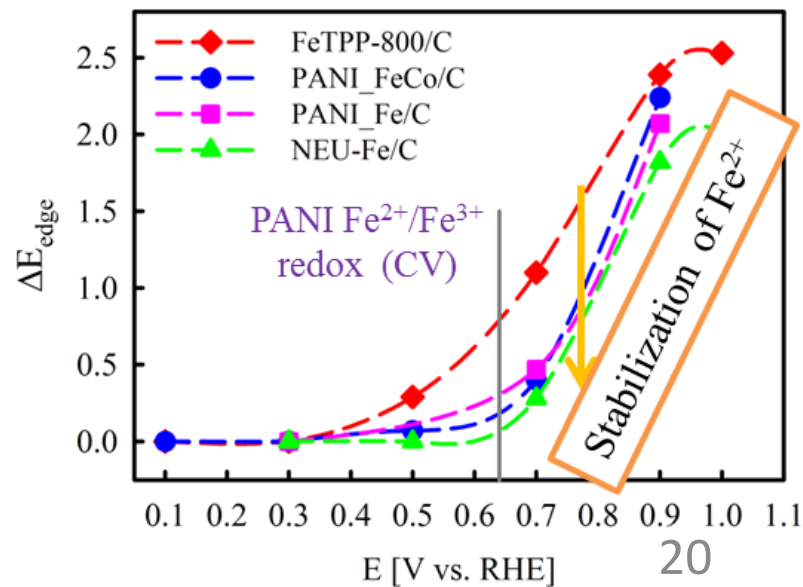
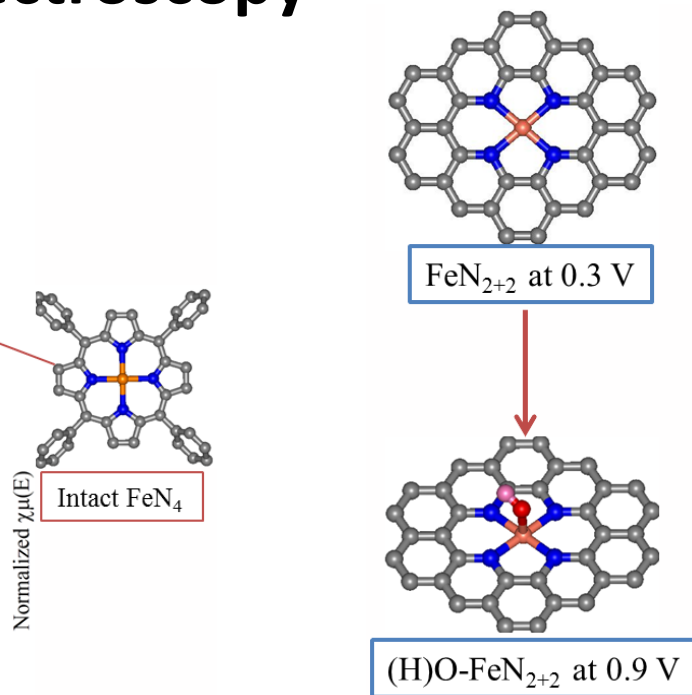
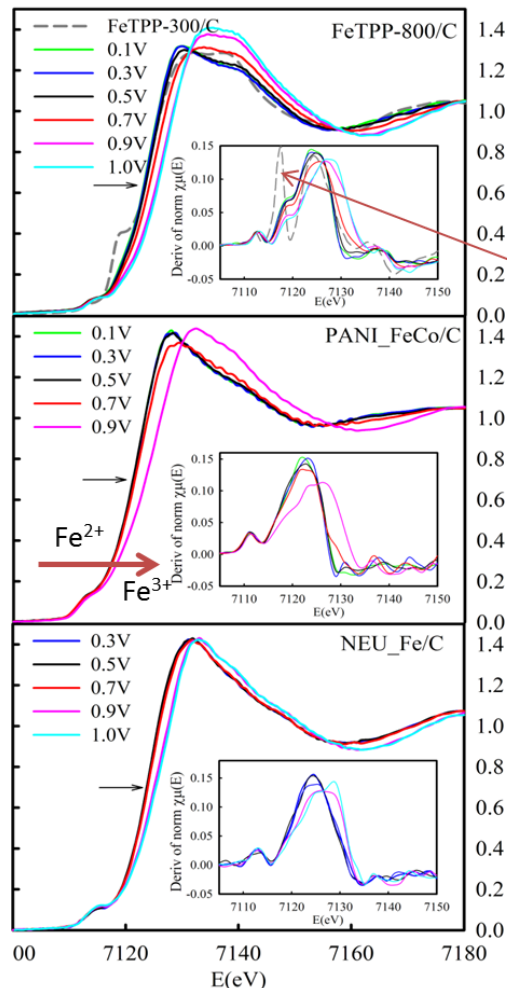
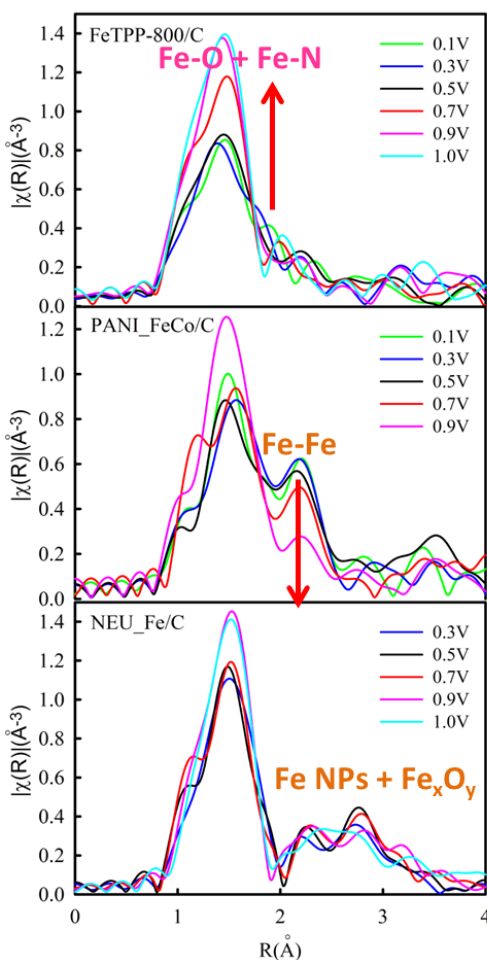


EXAFS		Fe8AA		Fe-CTS	
		Fe-N/C	Fe-Fe	Fe-N/C	Fe-Fe
CN	0.3 V	4.3±0.6	-	3.6±0.7	1.2±0.3
	0.9 V	5.2±0.8	-	4.0±0.8	1.3±0.3
R (Å)	0.3 V	2.07±0.02	-	2.02±0.02	2.51±0.01
	0.9 V	2.05±0.02	-	2.01±0.02	2.52±0.01

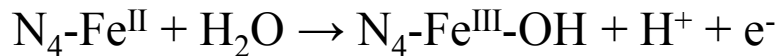
1. Fe8AA is dominated by Fe-N<sub>4</sub> sites; and Fe-CTS contains both Fe-N<sub>x</sub> and Fe<sub>3</sub>C.
2. Owing to the multiple-component nature of the Fe-CTS, the coordination number (x) of the Fe in Fe-N<sub>x</sub> sites is inconclusive. The CN determined by EXAFS (bulk average technique) is an average result of the CN in Fe-N<sub>x</sub> and the CN in Fe<sub>3</sub>C (N and C can not be distinguished by XAS as surrounding atoms).



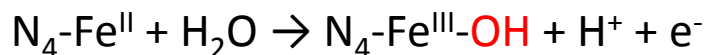
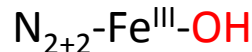
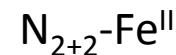
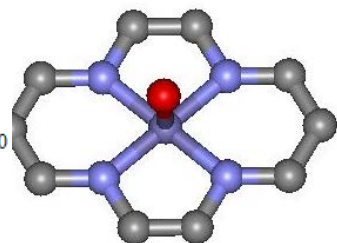
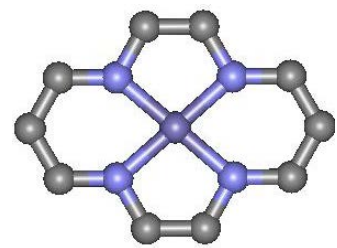
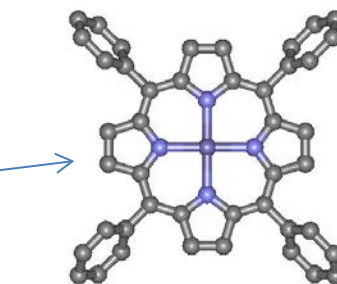
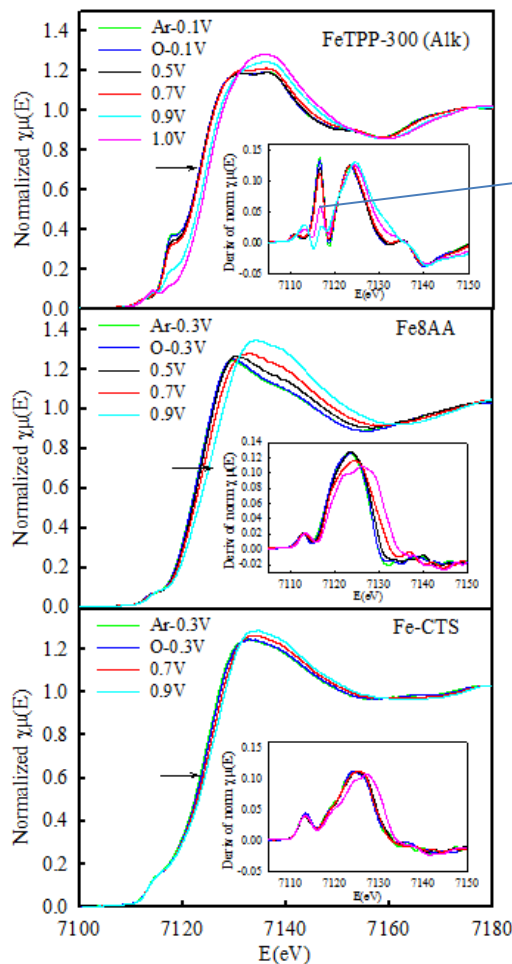
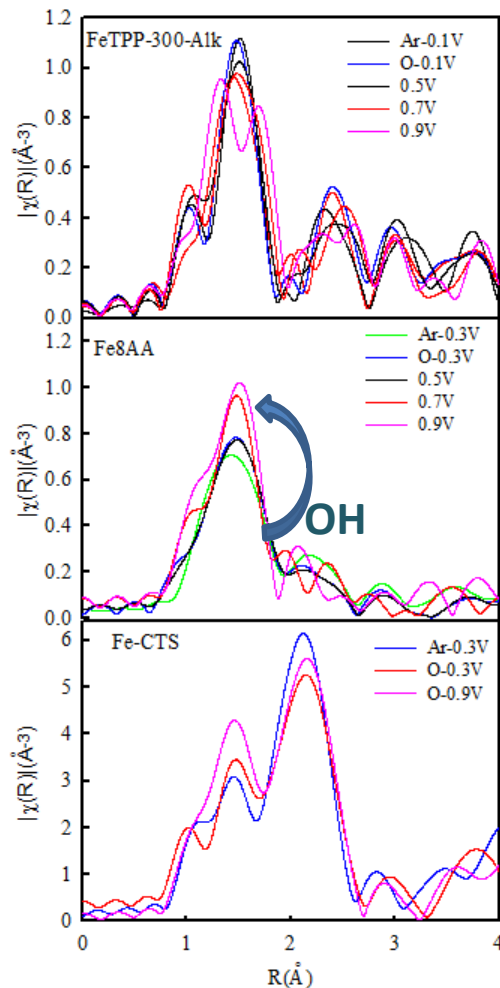
# Mechanistic Studies and Spectroscopy



The transition between Fe<sup>2+</sup> and Fe<sup>3+</sup> oxidation states is accompanied with the adsorption of OH.



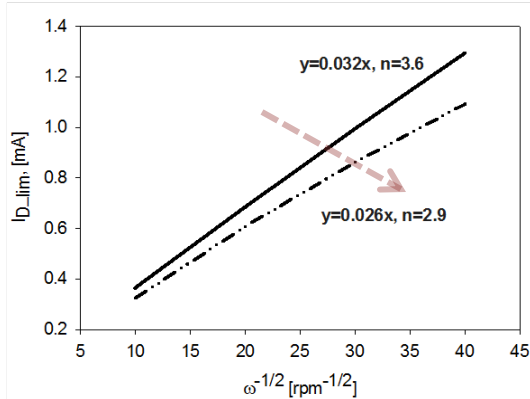
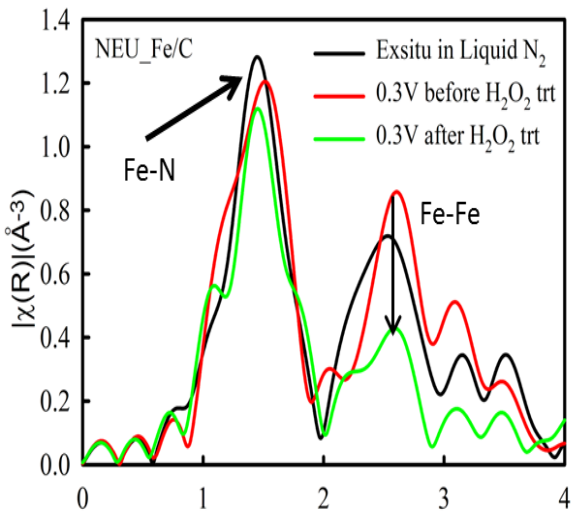
# ORR Kinetics: XANES+EXAFS Analysis



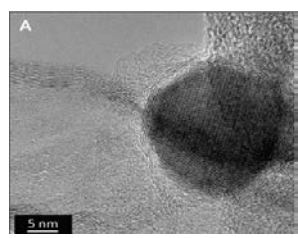
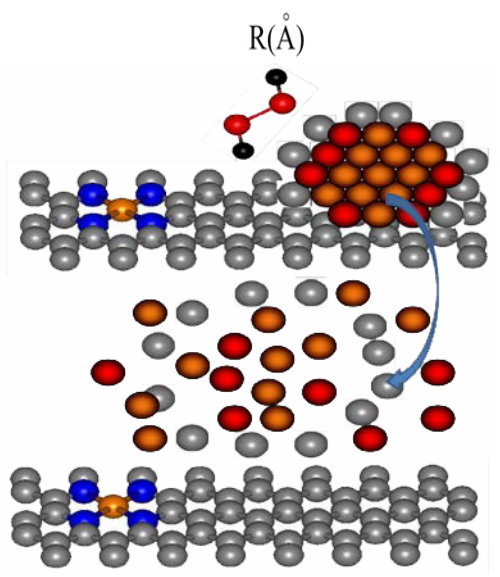
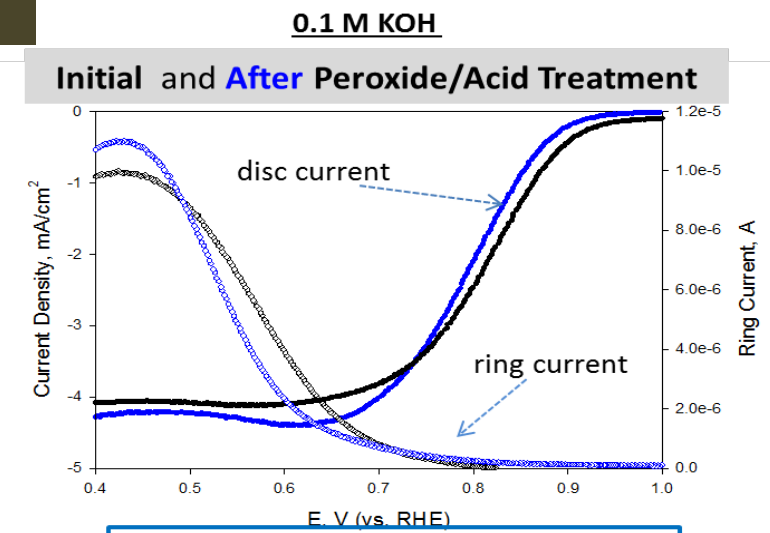
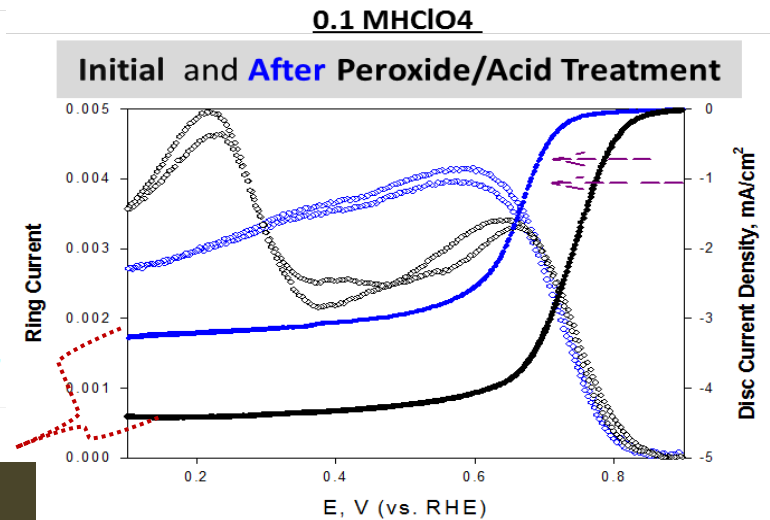
The increase of the first FT peak ( $\sim 1.5 \text{ \AA}$ ), as well as the XANES edge shift as a function of applied potential, are indicative of the Fe-N<sub>x</sub> as the active sites.

Acid versus Alkaline

Selective removal of Fe<sub>NPs</sub> => enhanced 2e ORR in acid & no effect in alkaline



less active sites available



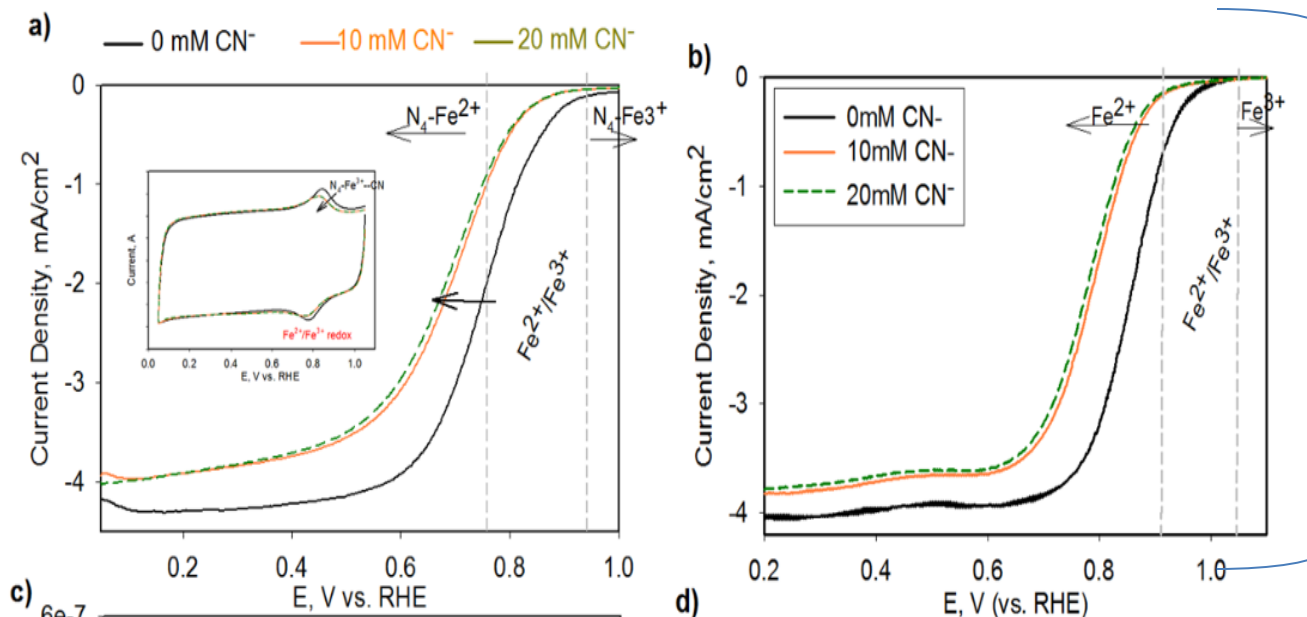
Sci. (2011); G. Wu, et al.

Peroxide attacks the graphene sheets that protect Fe/FeO<sub>x</sub> NPs.

Fe-N<sub>4</sub> sufficient for both O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> reduction in alkaline

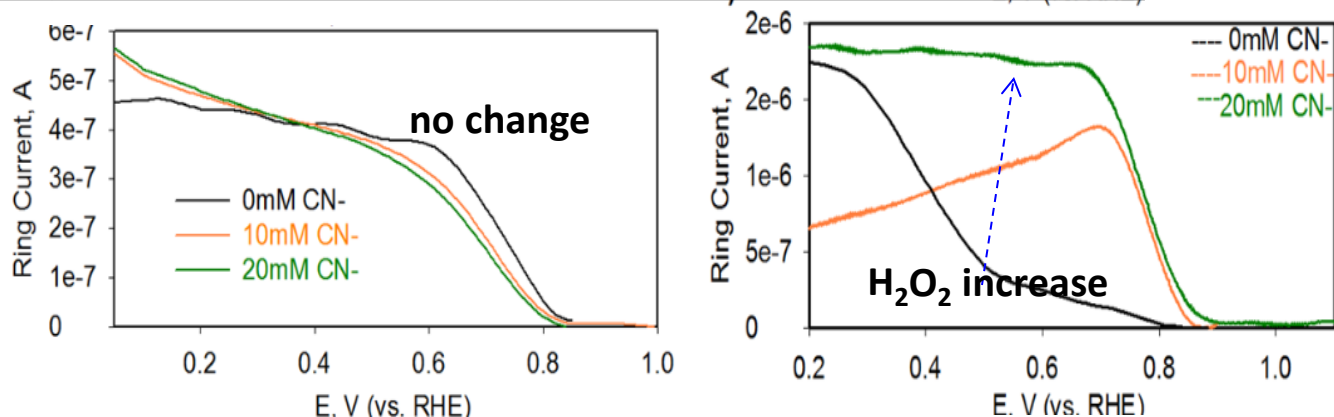
## Effect of Blocking of the Fe-N<sub>x</sub> Centers

ORR Polarization Curves in acid (left) and alkaline (right)



❖ CN<sup>-</sup> are known to be poisoned Fe<sup>3+</sup>N<sub>4</sub>

Ring current due to oxidation of peroxide intermediate formed during ORR

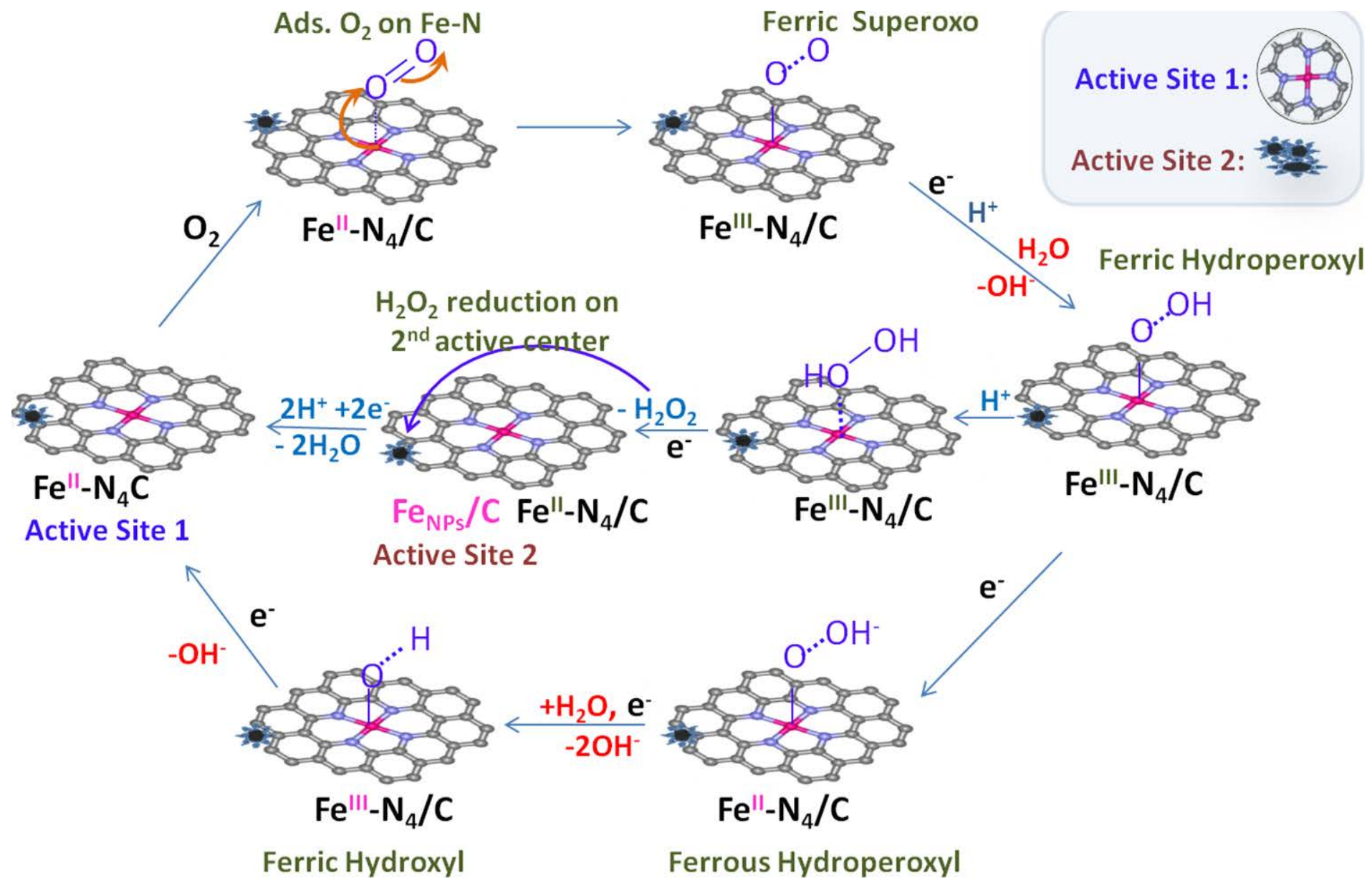


❖ Increase of H<sub>2</sub>O<sub>2</sub> formation due to blocking of the FeN<sub>4</sub> center

❖ FeN<sub>4</sub> the site able to reduce H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O

Negative shift of polarization curve in both media, but change of mechanism only in alkaline

# ORR Mechanism in Acid versus Alkaline Media...





# Summary

- Task 1.1 Design of Materials as High Performance Catalysts: These have lead to several candidates meeting DOE target of 150-400 A/cm<sup>3</sup> and 100 mA/cm<sup>2</sup> (iR free) at 0.8 V vs. RHE.
- ***DOE Go/No Go decision point successfully reached by down-selected UNM catalyst.***
- Task 1.2 Tailored Synthesis for Mechanistic Interpretation: This is progressing in concert with spectroscopy and computation leading to a concerted structure property relationship. This is 80 % complete, needing further confirmation and validation.
- Task 1.3 Catalyst Scale up: Initiated with Pajarito Powder LLC (Albuquerque, NM). The scale up effort is aiming to exceed the DOE goals by reaching 100-gram batch size at the end of the program with <5% variability (inter and intra batch).
- Task 2.1 Translation of volumetric activity to actual fuel cell performance levels with a target of 100 mA/cm<sup>2</sup> at 0.8 V (iR Free). Lowering of mass transport in the reaction and electrode structure is our current focus. Q1 and Q2 target for Air operation (30 mA/cm<sup>2</sup> @ 0.8 V (iR free) was met successfully.
- Task 2.2 Good catalyst durability has been reported. However pushing the limits of carbon stability causes severe activity decline. This task is 70% complete.
- Task 3. Good synergy has been reported to spectroscopy and computation with first ever report of a concerted understanding of structure property relationship. This task is 70% complete.

# Collaborations

## Partners (this project)

- Northeastern Univ., (Prime) Boston, MA: S. Mukerjee (P.I.)
- Univ. of New Mexico, Albuquerque, NM: Prof. P. Atanassov (university subcontractor)
- Michigan State University, East Lansing, MI: Prof. S. Barton (university subcontractor)
- Pajarito Powder, Albuquerque, NM: P. Short and B. Halevi (industry subcontractor)
- Nissan Technical Center North America, Detroit, MI: Dr. N. Dale (industry subcontractor)
- Los Alamos National Lab, Los Alamos, NM: Dr. P. Zelenay (Federal lab subcontractor)

## Other collaborators:

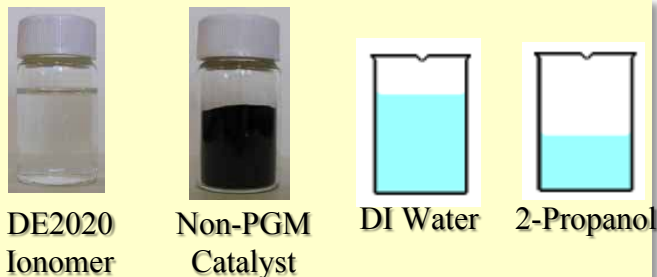
- Jean-Pol Dodelet: Canetiq, Canada (non-funded collaborator)



# Technical Back-Up Slides

# UNM Catalyst MEA Testing at NTCNA

## Methods: GDE and MEA Fabrication

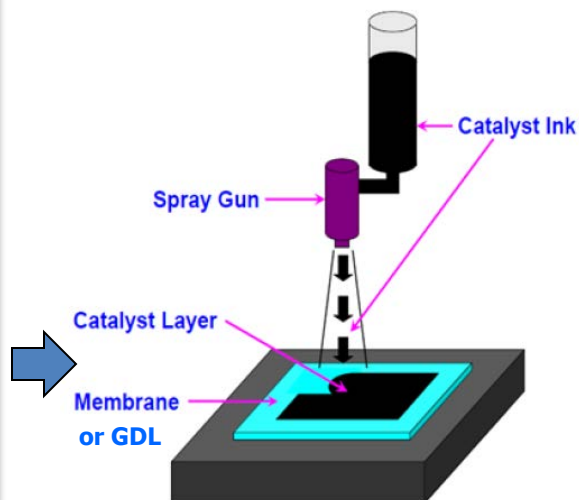


Catalyst Ink Preparation

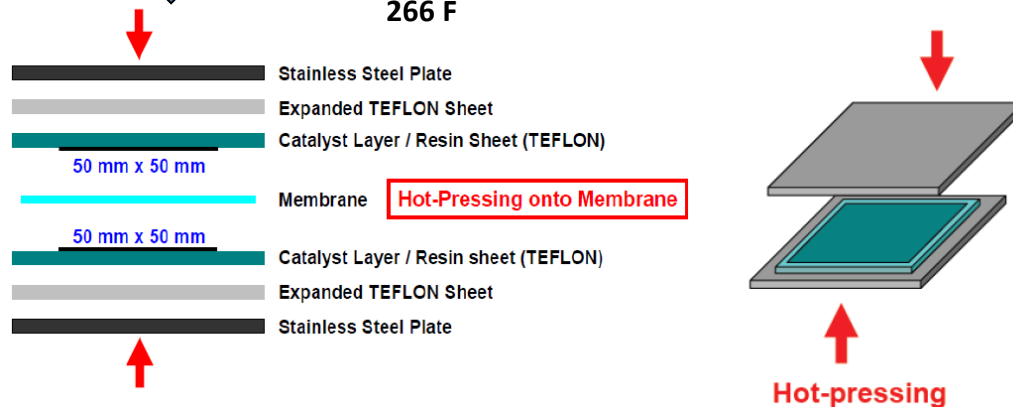


IKA Homogenizer  
(4 hours at 10,000 rpm)

### Robotic Spray Deposition System



### Hot-Pressing GDE onto the Membrane 266 F






## Milestone- DOE Go/No Go Decision

### Task 2. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

#### MEA Validation Test Performed at NTCNA on UNM CTS Catalysts

##### Optimization of UNM Ink Recipe

- The optimized I/C ratio for this catalyst is unknown.
- Three different I/C ratios were used in order to establish a trend and find an optimal/ideal value.

MEA	UNM CTS 35% Nafion	UNM CTS 45% Nafion	UNM CTS 55% Nafion
Symbol			
Actual Catalyst Loading	4 (C), 0.4 (A) mg/cm <sup>2</sup>	4 (C), 0.4 (A) mg/cm <sup>2</sup>	4 (C), 0.4 (A) mg/cm <sup>2</sup>
I/C ratio	0.54 (35% ionomer)	0.82 (45% ionomer)	1.2 (55% ionomer)
Description	NTCNA hot-pressed using JM GDE+ NTCNA sprayed UNM GDE + NRE 211		
Active area (C)	25 cm <sup>2</sup>		
GDL	SGL GDL 25BCH		

- JMFC 0.4 mg<sub>Pt</sub>/cm<sup>2</sup> GDE was used as an anode
- Straight flow field and updated protocols were used in this study
- Same assembly pressure (1.1 Nm) was applied for all MEAs
- Modified NTCNA hot-pressing conditions were used




# UNM CTS-AAPyr Catalyst – MEA Testing

## Experimental



### Details of MEA Testing at NTCNA

- NTCNA jointly tested two catalysts supplied by University of New Mexico (UNM) in Feb/March 2014
- These two catalysts were blends of their two previous catalysts: CTS and AAPyR
- These two catalysts are different combination ratios of CTS and AAPyR
  - CTS-AAPyr 70%:30%
  - CTS-Aapyr 50%:50%
- The optimized I/C ratio found last year (2013 results) was used as the starting point for this year's MEA tests. Other I/C ratios may be used in the future to establish a trend and find an optimal/ideal value.

MEA	2014 CTS-AAPyr 70:30	2014 CTS-AAPyr 50:50	2013 CTS
Symbol			
Nafion loading	55%	55%	55%
Actual Catalyst Loading	4 (C), 0.4 (A) mg/cm <sup>2</sup>	4 (C), 0.4 (A) mg/cm <sup>2</sup>	4 (C), 0.4 (A) mg/cm <sup>2</sup>
I/C ratio	1.2	1.2	1.2
Description	NTCNA hot-pressed using JM GDE+ <b>NTCNA sprayed</b> UNM GDE + NRE 211		
Active area (C)	25 cm <sup>2</sup>		
GDL	SGL GDL 25BCH		

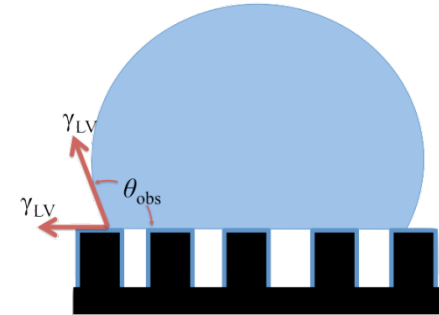
- JMFC 0.4 mg<sub>Pt</sub>/cm<sup>2</sup> GDE was used as an anode
- Straight flow field and updated protocols were used in this study
- Same assembly pressure (0.9 Nm) was applied for all MEAs
- Modified NTCNA hot-pressing conditions were used

# Modeling and Optimization

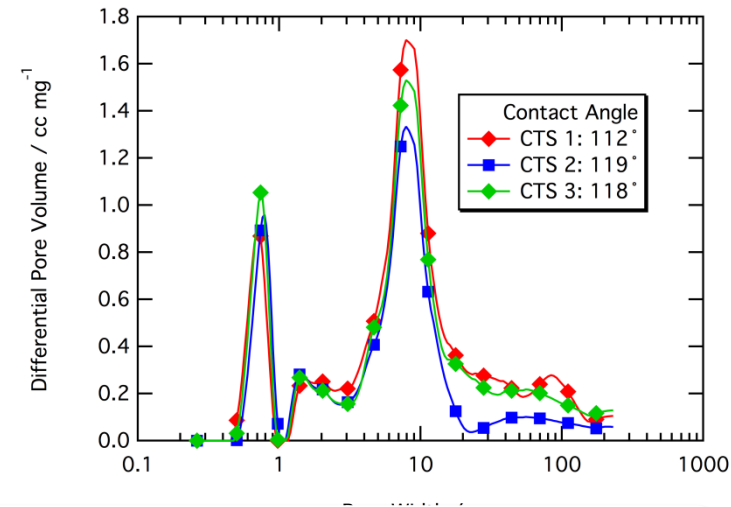
- Optimize performance in Air
- Quantify effects on performance:
  - Mesoporosity
  - Hydrophobicity
  - Conductivity (ionic & electronic)
- Active surface area,  $A_{act}$ , modified by
  - Ionomer intrusion,  $f_e$ ,
  - Saturation,  $S$
- Cassie model for receding contact angle,  $\theta_{obs}$ :
  - $\phi$ : fraction of the surface in contact with liquid, determined by combined **water vapor adsorption** and **nitrogen physisorption**.

$$A_{act} = A_{exp} f_e (1 - S)$$

$$\cos(\theta_{obs}) = 2\phi - 1$$



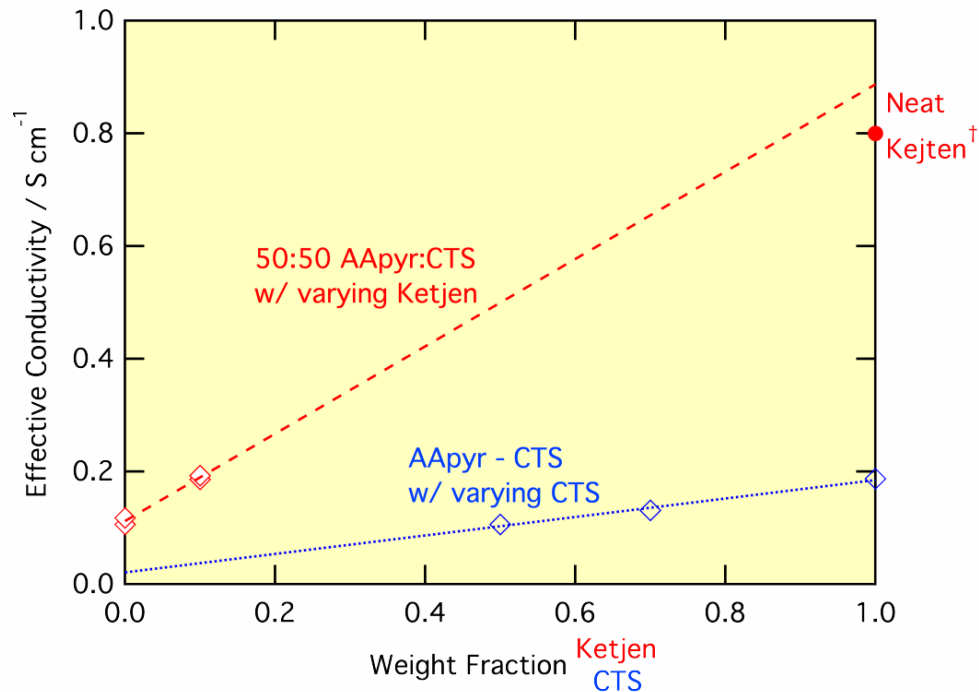
The Receding Cassie Model for Hydrophobicity: a thin layer of liquid eliminates the solid-vapor interface.



Area ratio,  $\phi$ , and contact angle,  $\theta_{obs}$ , estimated from PSD.

# Effect of Composition on Catalyst Layer Conductivity

Conductivity estimated from measured catalyst layer resistivity



<sup>†</sup> Chung et al J Appl. Phys. 1982

- Ketjen conductivity 8-fold higher than AApyr, 4-fold higher than CTS
- Estimated conductivity follows expected linear trend.