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

2015 DOE Hydrogen and Fuel Cell Program Review
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Project ID# FC086

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Overview Slide

- **Timeline:**
  - Start date: 8/01/2010
  - End date: 7/31/2015

- **Budget Data:** Total Funding Spent as of 3/31/2014:
  - Total Project Value: $4,942,301 (Federal), $1,437,714 (cost share); Total $6,38015
  - Cost Share Percentage: 20%
  - Total DOE Funds Spent*: $4672,824
  * As of 3/31/15

- **Barriers/Targets (Addresses both ‘Cost’ and ‘Durability’)**
  - **Key Barriers:** Elevating inherent mass activity (at 0.85 to 0.9 V) and areal activity in Air (0.65 V) to approach DOE FCTO PGM 2020 targets.
  - **Activity Targets:** for Non-PGM catalysts (BP-1): Volumetric activity: to exceed 300 A/cm³ (2015-target) and Areal Activity: 100 mA/cm² at 0.8 V 1.5 bar total pressure. (BP-2): Areal Activity (Air): 30 mA/cm² at 0.8 V (Q2, FY-14) and 1.0 A/cm² at 0.4 V (Q5-FY-15) in H₂/Air 2.5 bar total pressure.
  - **Durability Target:** at temperatures ≤ 80°C, Non-pgm catalysts subjected to 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/cm².

- **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
Relevance

- **Objectives:** To develop new classes of non-PGM electrocatalysts which would meet or exceed 2015 project targets for activity and durability. 2015 Project Activity targets are 100 mA/cm² (H₂/O₂, 1.5 bar total pressure) and 30 mA/cm² @ 0.8 V and 1 A/cm² at 0.4 V (H₂/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 H₂ 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**
    - 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:**
  - Meeting and Exceeding Program Areal Activity Target of 30 mA/cm² @ 0.8 V and 1 A/cm² @ 0.4 V, non iR corrected, H₂/Air, 80ºC, 2.5 bar total pressure, 100% RH
    - (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.
Approach: Program Management and Implementation

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

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

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

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

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

Automotive Test Protocols, Stack Testing and Durability Validation (NTCNA)
Thrust Area 5-Task 2.4
Quarterly Milestones Q3 FY14-Q3 FY15

• Q2 (FY 14): 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 ≤ ± 5%.

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

• Q3 (FY 14): 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.

• Q4 (FY 14): Using non-pgm cathode catalysts, demonstrate MEA performance of at least 30 mA/cm² at 0.8 V in H₂/Air, 2.5 bar total pressure.

• Q1 (FY 15): Non-pgm catalysts subjected to catalyst stability (<10% of initial activity) 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/cm².

• Q2 (FY15): 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.

• Q3 (FY15): With a cathode optimized for non-pgm catalysts, achieve MEA performance of at least 1.0 A/cm² at 0.4 V in H₂/Air, 2.5 bar total pressure.

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

- **Mechano-Chemical Approach (UNM)**

  ![Nicarbazin](image)

  + Fe-Salt + Silica templated

  → **Ball milling**

  → **Pyrolysis**

  → **UNM-CTS**

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

  ![Aminoantipyrine](image)

  + Fe-Salt + Silica templated

  → **UNM-CTS**

- **Metal Organic Framework Approach: (NEU)**

  ![Metal Organic Framework](image)

  + Fe(NO₃)₃, DMF, 140°C, 120 h

  → **MOF + Encapsulated N-Precursor and Metal Salt**

  → **UNM-Fe-MOF**

  → **NEU-Fe-MOF**

[1] M=Fe, Co; X=C₂H₅O₂, Cl

[2] '@' indicates chemical encapsulation of phenanthroline and metal (M-N₄ active site)
Fe-CTS Modification for Air and Scale Up

- UNM SSM method Fe-CTS catalyst porosity modified for air operations and scaled to 200gram per batch
Stability & Degradation Mechanism of Fe-CTS

- Catalyst stable at 0.65V for 100+ hrs
  - surface oxidized, some active sites lost, slight collapse of pores and roughening
Fe-MOF tech Transfer and Scale Up

- Key process steps and variables established and being adjusted for x20 scale
- Promising performance of initial x10 batches established
Mass Transport Studies: Modeling and Experiments

- Accounts for **hydrophilicity** and **pore size distribution** in catalyst layer. UNM CTS catalysts
- Scaled up by PPC
- Fit to PPC MEA Data

Dominant Parameters:
- Hydrophobicity (All Potentials)
- Loading (low potentials)

**Fit to PPC MEA Data**

- Thin electrodes are optimal at low potential.

Temp. 80 C, 25BC GDL, 4mg/cm² Catalyst Loading, 45 wt% Nafion®, Cell Area: 5cm², membrane: NR211.
Helox Transport Study

- Study transport in catalyst layer with varying carrier gas (He, N₂, Ar) and diffusivity.
- O₂ consumption <20%, amenable to 1D model.
- Transport losses in both flow channel and Catalyst layer.

Diffusion boundary layer, $\delta \propto \sqrt[2]{\text{VFR}}$

Fit to Experiment (NEU MOF) for two carrier gases

Channel losses vary as $\text{VFR}^{-\frac{1}{2}}$
The stability of NEU-MOF catalyst was evaluated under Nissan load cycling and start-stop cycling protocols.

Protocols for Nissan and DOE Durability Working Group

- **Temperature (°C)**: 80 80
- **Gas condition Cathode**: N₂ N₂
- **Gas – Anode**: H₂ H₂
- **Voltage scan (V)**: [0.6, 1.0] [1.0, 1.5]
- **Scan rate (mV/s)**: 6s/cycle 500
- **Catalyst loading (mg/cm²)**: 0.6
- **No of cycles**: 10,000 1000

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.

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

- **Load Cycling**

- **Start-stop Cycling**
Mechanistic Studies and Spectroscopy

Participating Institutions:

UNM - XPS Studies

NEU - In situ Spectroscopy with Synchrotron Measurements

MSU - Macroscopic Modeling
Ambient Pressure XPS – 2.5 nm
Direct evidence of oxygen binding at the FeN$_x$ site

Metal-containing Fe-N-C catalyst

Metal-less N-C catalyst

In the case of metal-containing catalysts:
Rearrangement is occurring where Pyridinic N and FeN$_x$ sites contribute.

In the case of metal-less catalysts:
Rearrangement is occurring where graphitic and quaternary contribute.

- Rearrangement of Nitrogen spectra due to Oxygen (O$_2$) binding
- Shifting the position of Nitrogen peak to higher Binding Energies (BE)
- Most prominent effect explicitly associated with FeN$_x$ sites
Two major sites identified by *in situ* XAS

The two major types of sites in heat-treated Fe-N-C catalysts can be clearly distinguished by *in situ* XAS.

The local geometry, and relative content of each site can be quantitatively determined by EXAFS fitting.

This information facilitates to have controls over the content of the catalysts by controlling the precursors and the preparation procedures.
The transition between Fe$^{2+}$ and Fe$^{3+}$ oxidation states is accompanied with the adsorption of OH.

\[ \text{N}_4\text{-Fe}^{\text{II}} + \text{H}_2\text{O} \rightarrow \text{N}_4\text{-Fe}^{\text{III}}\text{-OH} + \text{H}^+ + \text{e}^- \]
Fe-N Switching behavior

EXAFS Analysis

XANES Analysis

The underlying fifth ligand was confirmed by XAS in combination with FEFF calculations. DFT suggests it drastically increases ORR activity.

Three dissimilar Fe-N switching behavior found in three different Fe-N\(_x\)-C active sites.
Stability: Peroxide treatment

70 mM H$_2$O$_2$ in 0.1 M HClO$_4$ cycled between 0.0 and 1.0 V, 250 cycles, 20 mV/s
Spectroscopic observations of the chemical moieties

57Fe Mössbauer Spectroscopy

UNM Fe-AApyr catalyst

UNM Fe-Nacarbazin catalyst

NEU-MOF
• Task 1.1 Design of Materials as High Performance Catalysts: These have lead to several candidates meeting DOE target of 150-400 A/cm³ and 100 mA/cm² @ 0.8 V (iR free), H₂/O₂, 1.5 bar total.

• 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 90% complete, MNOF derived material needs further investigation.

• 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 gm batch size at the end of the program with <5% variability (inter and intra batch).

• Task 2.1 Actual fuel cell performance levels with Air, with a target to 30 mA/cm² at 0.8 V and 1 A/cm² at 0.4 V (non iR corrected) H₂ /Air, 2.5 bar total pressure. Lowering of mass transport in the reaction and electrode structure is our current focus. Q4 and Q5 target for Air operation 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 80% 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 90% complete.
Future Activities

• Strategies for MOF derived catalyst scale up to 50 gm batch size with < 5% variability in H$_2$/Air MEA performance.
• Final validation of MOF derived catalyst at NTCNA for performance and durability.
• Advanced interfacial studies to investigate peroxide initiated free radical formation on various non PGM catalysts
• Advanced electrode and microporous layer design for enhanced mass transport.
Technology Transfer Activities

1. **Patents and Provisional Patents Filed:**

**Publications:**


**Patents:**


Technology Transfer Agreements in place with PPC between UNM and NEU groups for scale up.
Collaborations

Partners (this project)
- Northeastern Univ., (Prime) Boston, MA: S. Mukerjee (P.I)
- Univ. of New Mexico, Albuquerque, NM: Prof. P. Atanassov (Univ., subcontractor)
- Michigan State University, East Lansing, MI: Prof. S. Barton (Univ., subcontractor)
- Pajarito powders, Albuquerque, NM: P. Short and B. Halevi (Industry subcontractor)
- Nissan Technical Center North America, Detroit, MI: Dr. N. Dale (Industry, subcontractor)

Other collaborators:
Dr. Piotr Zelenay, Los Alamos National Laboratory
Jean-Pol Dodelet: Canetiq, Canada
Frederic Jouen, University of Montpelier, France
Critical Assumptions and Issues

• XAS data used for building active site models are based on assumptions inherent in the FEFF code. Careful control experiments have been used to validate the reported results.

• All iR corrections performed on fuel cell data was conducted using high frequency resistance measurements at 1 kHz.
Technical Back-Up Slides
### Governing Equations (Electrode-Scale)

#### B.C. I

<table>
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<td>$V_e</td>
<td>_I = I_e</td>
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<td>$N_L</td>
<td>_I = I_i</td>
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</tr>
<tr>
<td>$x_i</td>
<td><em>II = x</em>{i,bulk}$</td>
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#### Electrolyte Membrane

$$0 = -\kappa_s \nabla^2 V_s + nF r_{ORR}$$

#### Channel

$$0 = -\kappa_e \nabla^2 V_e - nF r_{ORR}$$

$$0 = -\frac{\kappa}{\mu} \nabla^2 P_i + 2r_{ORR} | x - r_{evap} | x$$

$$0 = -\nabla N_w + r_{evap} | x$$
Observation: direct correlation of FeN$_x$ sites and E$_{1/2}$ on one side, and analogous correlation for the pyridinic Nitrogen-containing moieties with E$_{1/2}$.
Pyridinic Nitrogen is a marker for **edge plane defects**.

Peak due to pyridinic Nitrogen is where disordered FeN$_x$ centers contribute.

In metal-less catalysts (no FeN$_x$ centers) – pyridinic catalyzes H$_2$O$_2$ → H$_2$O.
Start/Stop Cycling

Potential (V) vs RHE

0.2 0.4 0.6 0.8 1.0

Current Density (mA/cm²)

-6 -5 -4 -3 -2 -1 0

Initial
After 6,700 cycles

%H₂O₂

0.0 0.5 1.0 1.5 2.0 2.5 3.0

Potential (V) vs RHE

0.2 0.4 0.6 0.8 1.0 1.2

Current (mA)

-0.6 -0.4 -0.2 0.0 0.2 0.4 0.6

C-Corrosion Cycled

E(eV)

7110 7120 7130 7140 7150 7160

Initial
Normalized i(E)

χµ(E)

0.0 0.2 0.4 0.6 0.8 1.0

Normalized i(E)

1.0 0.8 0.6 0.4 0.2 0.0

C-Corrosion Cycled

0.1V

0.9V

R(Å)

0 1 2 3 4 5

270 mV

R(A-3)

Normalized χ(E)

0.1V

0.9V

Δµ = 0.9 V - 0.1 V

Normalized χ(E)

0.0 0.04 0.08 0.12 0.16 0.20 0.24 0.28 0.32

Normalized χ(E)

0.0 0.02 0.04 0.06 0.08 0.10

Normalized χ(E)

0.0 0.02 0.04 0.06 0.08 0.10

Normalized χ(E)
Central Iron displacement as evidenced by XAS + FEFF

EXAFS plus FEFF9 calculations give the first evidence of the central iron displacement in the pyrolyzed samples, and samples with bigger displacement appears to show better ORR activity.