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Innovative Non-PGM Catalysts for High-Temperature PEMFCs

2017 DOE Hydrogen and Fuel Cell Program Review

PI: Sanjeev Mukerjee

Department of Chemistry and Chemical Biology,

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

June 7th, 2017

Project ID# FC132

Overview Project [DE-EE0006965]

- **Timeline**:
  - Start date: 7/01/2015
  - End date: 12/31/2017
- **Budget Data**: Total Project Value: $ 1,029,493 (Federal), $ 257,373 (cost share); Total $ 1,286,866
- Cost Share Percentage: 20%
- **Barriers/Targets (Addresses both 'Cost' and 'Durability')**
  - **Key Barriers:** Current state of the art PAFC imbibed systems use 3-5 mg/cm^2 amounting to $ 750-1000/KW in noble metal cost. Other issues relate to elevated mass transport losses due to six fold lower O_2 permeability and proton conduction.
  - **Activity Targets**: for PGM-free catalysts (**BP-1**): Areal Activity (Air): 200 mA/cm^2 at 0.6 V, 2.5 bar total pressure with PGM content (anode) lower than 1.5 mg/cm^2 (go/no go point).
  - **Durability Target**: at temperatures ≤ 180°C, PGM-free catalysts subjected to OCV test for 3 hrs with less than 3% loss at 0.65 V. Chronoamperometric test at 0.8 V for 48 hrs with less than 3% loss at 0.65 V.
- **Partners**
  - *Northeastern Univ*., (Prime) Boston, MA: S. Mukerjee (P.I)
  - *Univ. of New Mexico (Sub-awardee)*, Albuquerque, NM: Prof. P. Atanassov
  - *Pajarito Powder (Sub-awardee)*, Albuquerque, NM: Dr. B. Zulevi
  - *Advent North America (special materials supplier/vendor),* Boston, MA: Dr. Emory De Castro

Relevance

- **Objectives:**
  - To investigate the use and development of PGM-free electrocatalysts that would allow for high performance in high-temperature proton exchange membrane fuel cells.
- **Relevance to DOE Mission:**
  - This will enable decoupling HT-PEM technology from Pt resource availability and lower MEA costs by at least 50%.
    - Significant benefits to energy efficiency, carbon footprint, and United States energy security
- **Impact:**
  - Reduction of unit cost from $30-50k to <$10k for micro combined heat and power devices (micro-CHP).
  - Independence from Pt and other precious metal global availability
  - Greater tolerance to poisons which typically effect Pt & Pt alloys (i.e., sulfur, CO, phosphate, etc.), Hence ability to tolerate H_2 with greater impurity.

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Overall Approach

- <u>**Overall technical approach**</u>:
  - **New Catalyst development and scale up strategies:**
    - **Iron-Nitrogen-Carbon based active sites embedded in a MOF structure**
      - Scale up through unique reactive ball milling approach
        - Simultaneous ball milling of all precursors (Fe salt, chelating agent, Zn nitrate, imidazole
    - **Improvement of mass transport and corrosion resistant characteristics**
      - Through use of sacrificial support method (SSM)
      - Through the use of alternative support materials including TaC_x and WC_x
  - **Enhanced understanding of mass transport through modeling and mass transport experiments (Hel-ox)**
    - Low concentration oxygen gases used for evaluating mass transport parameters
  - **Single cell fabrication and testing**
    - For elucidating performance as well as durability/corrosion resistance information
- <u>**Program Technical Barriers and Approach to Overcome them**</u>:
  - Meeting and Exceeding Program targets of 100mA/cm^2 @ 0.7V (H_2/O_2, 1.5bar total pressure) & 200mA/cm^2 @ 0.6V (H_2/air, 2.5bar total pressure).
    - (a) New classes of materials due to current high precious metal loadings (2-4mg/cm2), which cause precious metal costs of $750-1000/KW (with 200mW/cm2 @ 0.7V, H2/air, 2.5bar total pressure)
    - (b) Redesign of the catalyst support and Electrode Structure for efficient mass transport.
      - High mass transport losses due to lower O_2 (5x) and proton (6x) permeability
    - (b) Developing materials to avoid phosphate poisoning effects present with precious metals

Milestone Summary Table							
Recipient Name	Northeastern University (NEU), Sanjeev Mukerjee (P.I)						
Project Title	Innovative Non PGM Catalysts for CHP Relevant Proton Conducting Fuel Cells						
Task Number	**Task or Subtask Title**	**Milestone Type**	**Milestone or Go/No Go Decision Point**	**Milestone Description (Go/No-go Decision Criteria)**	**Milestone Verification Process**	**Anticipated Quarter**	
						Date	Quarter
1.1	Catalyst Preparation and scale up with MOF chemistry.	Milestone	M1.1a	Develop scale up chemistry based on reactive ball milling for achieving 5 gm batch of MOF-based non-PGM cathode catalyst material.	Less than 5% inter and intra batch variation in in RDE performance using 0.1 M $HClO_4$ with up to 100 mM H_3PO_4.	3 mo	Q 1
1.1	Catalyst Preparation and scale up with MOF chemistry.	Milestone	M1.1b	Demonstrate initial MEA activity of non-PGM cathode catalyst with PA-imbibed membrane.	Polarization measurements demonstrating 100 mA/cm^2 at 0.7 V using H_2/O_2 at 180^{o}C 1.5 bar total pressure.	6 mo	Q 2
2.1	Improving Mass Transport Characteristics.	Milestone	M2.1	MEA testing of SSM-templated non-PGM catalyst.	MEA performance of 200 mA/cm^2 at 0.65 V, H_2/Air, 180^{o}C, 2.5 bar total pressure.	9 mo	Q 3
1.2	Scale up of catalysts based on MOF approach.	Milestone	M1.2	Scale up of MOF-based non-PGM catalyst to 30-50 gm batch size.	Less than 5% inter and intra batch variation in RDE and MEA performance (H_2/Air)	12 mo	Q4

Go/No-Go Decision		Go/No-Go Decision	GNG 1	Fuel cell measurements and validation.	At least 200 mA/cm^2 at 0.60 V with 2.5 bar total pressure, H_2/air, 180^{o}C. Total PGM catalyst loading on the PA-imbibed membrane-based MEA to be lower than 1.5 mg/cm^2 Pt exclusive to the anode electrode with a non-PGM cathode.	12 mo	End of Q4
1.4	Durability studies	Milestone	M1.4a	Durability testing on scaled up samples based on reactive ball milling (30-50 gm batch).	MEA performance of 200 mA/cm^2 at 0.6 V, H_2/air, 180^{o}C, 2.5 bar total pressure. Chronoamperometric testing at 0.8 V (H_2/air) 2.5 bar total pressure (180^{o}C) with 5 % activity loss over 48 hrs.	18 mo	Q5
2.3	Durability studies	Milestone	M2.3a	Corrosion testing of SSM based materials from sub-task 2,3	Open circuit test on SSM based materials at 180^{o}C, H_2/air conditions for 3 hrs with activity loss of less than 3% at 0.65 V (2.5 bar total pressure).	21 mo	Q6
3.3	Final down select	Milestone	M3.3a	Down select of scaled up integrated material containing FE-MOF based active site, SSM based microporous layer on GDL structures	Achieving H_2/Air performance target of 200 mA/cm^2 at 0.65 V, 180^{o}C, 2.5 bar absolute pressure.	24 mo	Q7
3.2	Fuel cell test validation	Milestone	M3.2b	Fuel cell test validation at OEM partner facility with 100 cm^2 MEA using PA-imbibed membrane and non-PGM cathode catalyst.	Achieving H_2/Air performance target of 200 mA/cm^2 at 0.65 V, 180^{o}C, 2.5 bar total pressure	24 mo	Q8

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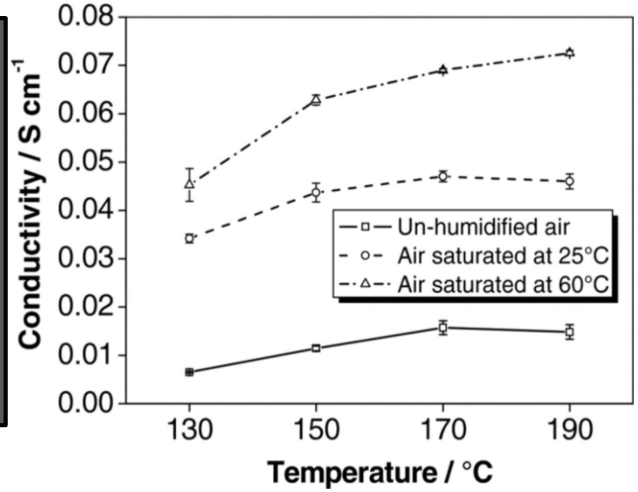
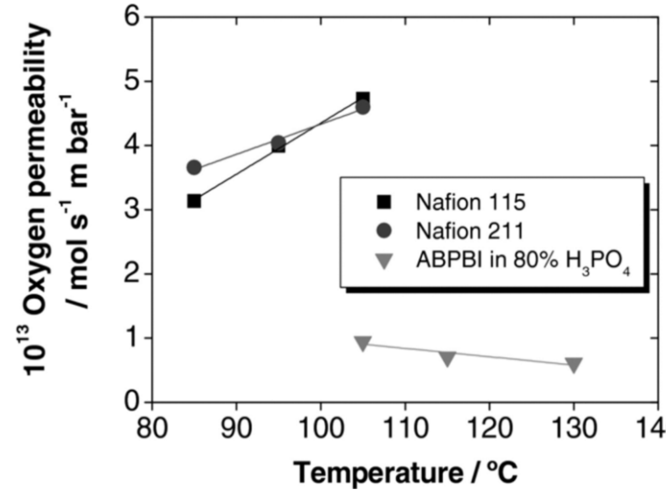
Running Hot and Dry: Poor Proton Conductivity and Oxygen Permeability in PA Systems

Fuel Cell Type	PAFC	PEM	PEM	MCFC	MCFC	SOFC
Nominal Electricity Capacity (KW)	200	10	200	300	1200	125
Operating Temperature (F°)	400	150	150	1200	1200	1750
Electrical Efficiency (% HHV)	33	30	35	43	43	43
Total CHP Efficiency (% HHV)	81	65	72	62	62	77

- Successfully commercialized for stationary power applications
- 10 year stack life and 20 year product life
- Operates at ~ 150-200°C
- 81% total CHP efficiency
- 90-100% Phosphoric Acid electrolyte
    - Durable Membranes Available
- Pt-based catalyst for anode and cathode Key Barrier





Linares J J et al. J. Electrochem. Soc. 2012;159:F194-F202

	Conductivity (S/cm)	λ (H_2O/SO_3)	D (10^6) (cm^2/S)	C (10^6) (mol/cm^3)	DC
Nafion	0.12	12.5	5.51	9.42	55.88

Balance of Plant
CO Tolerance: < 2% above 160°C
S Tolerance: 100 ppm
No need for Prox unit

Power Density
~ 400 mW/cm^2 at 0.65 V, H_2 /Air
Nafion: 1.1 W/cm^2

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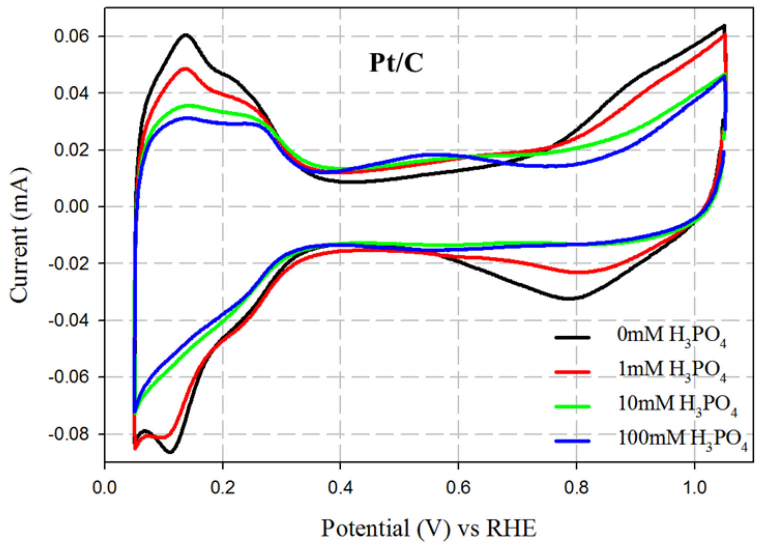
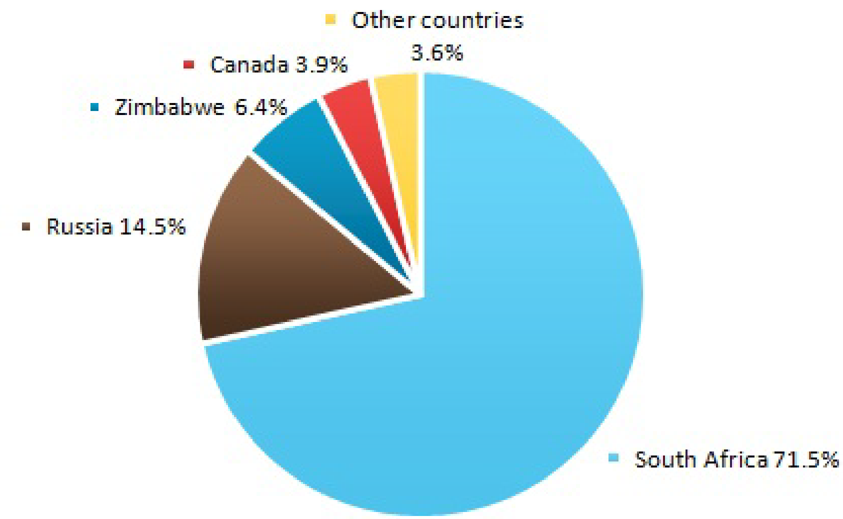
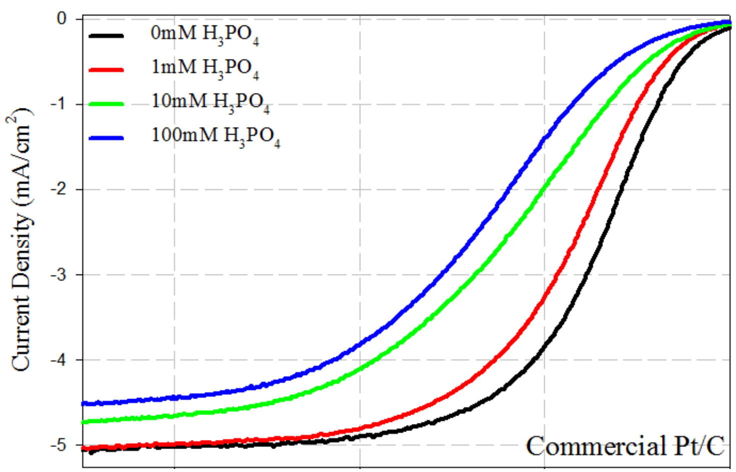
Phosphate Anion Poisoning & Platinum Requirements

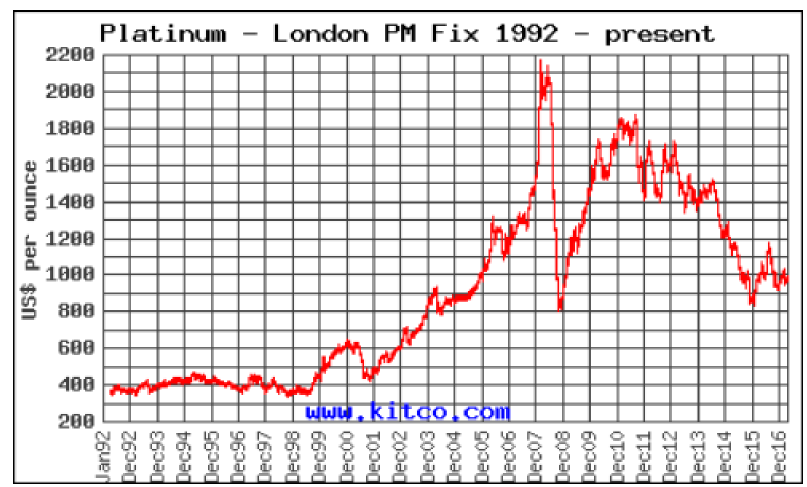


Global Platinum Production in 2012



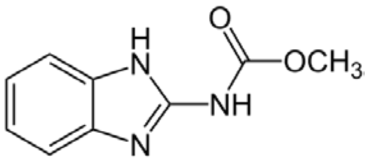


Average Global Platinum Cost Trend
Volatility is key issue



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

❖ **Mechano-Chemical Approach (UNM)**



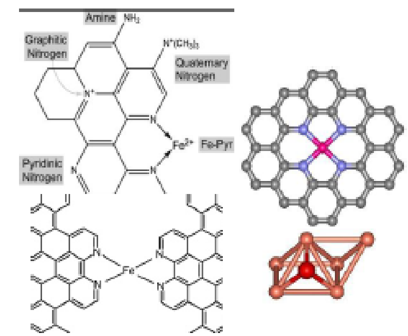
Carbendazim

+ Fe-Salt+ Silica templated

UNM-CBDZ

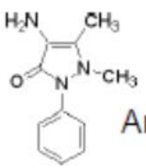
Ball milling

Pyrolysis



M-N-C catalyst

❖ **N-Chelating Precursor-Metal Salt Approach (UNM)**



Aminoantipyrine

+ Fe-Salt+ Silica templated

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

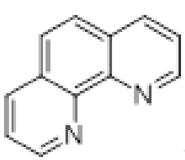
+ $Fe(NO_3)_3$, DMF, 140°C, 120 h

UNM-Fe-MOF

MeOH

rt

2h

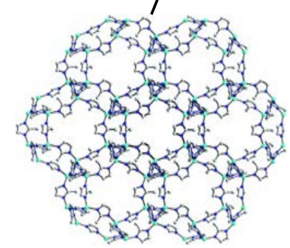


MeOH/ H2O

+ MX_2[1]

$Zn(NO_3)_2.6H_2O$

MOF + Encapsulated N-Precursor and Metal Salt

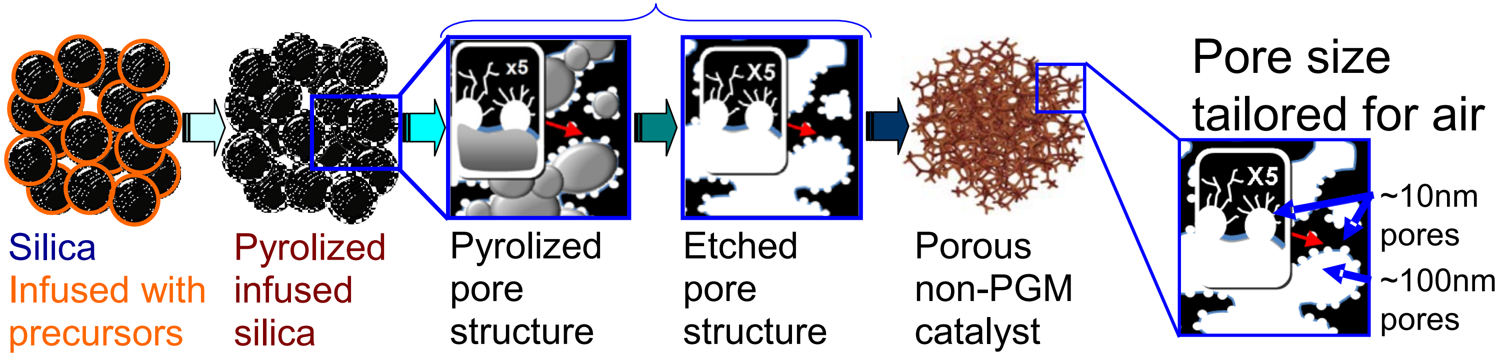


NEU-Fe-MOF

[1] M=Fe, Co; X=$C_2H_3O_2$, Cl

[2] '@' indicates chemical encapsulation of phenanthroline and metal ($M\text{-}N_4$ active site)

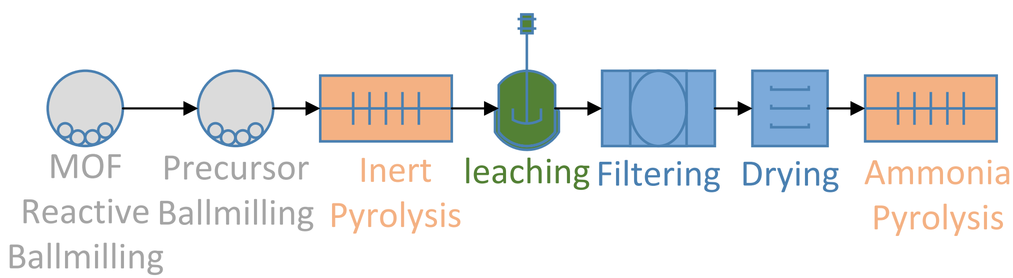
Fe-CTS Modification for Air and Scale Up

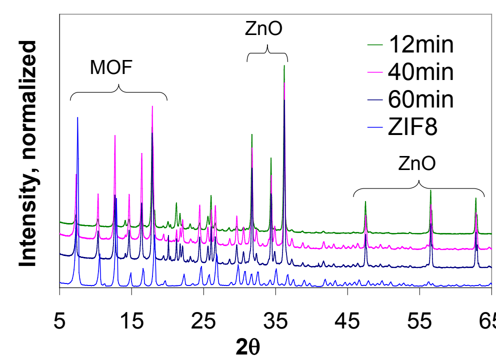


- **UNM SSM method Fe-CTS catalyst porosity modified for air operations and scaled to 200gram per batch**

Fe-MOF tech Transfer and Scale Up

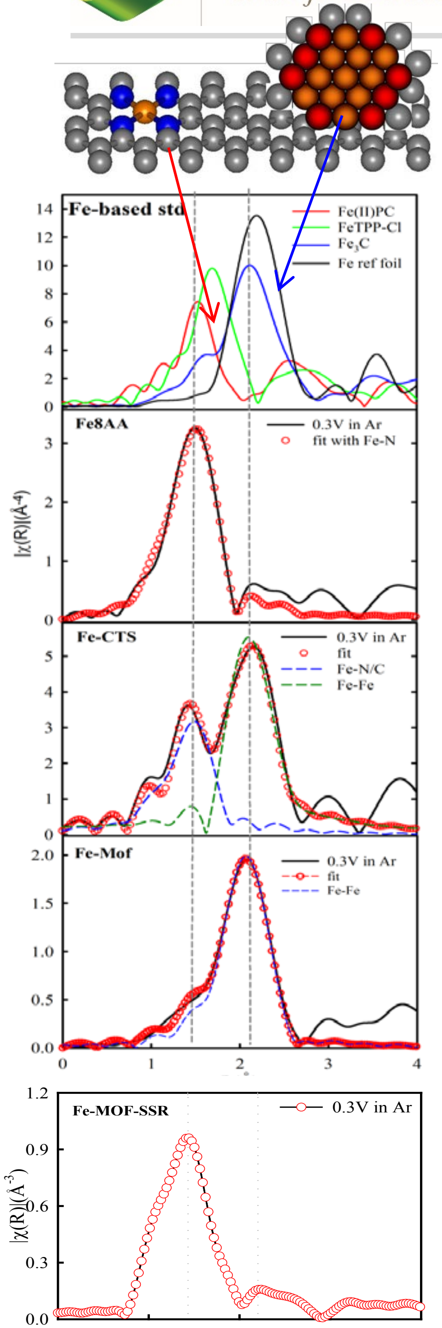
Reactive Milled MOF processing established

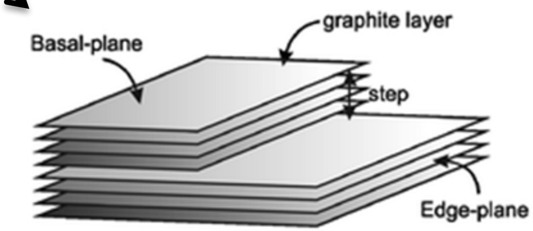


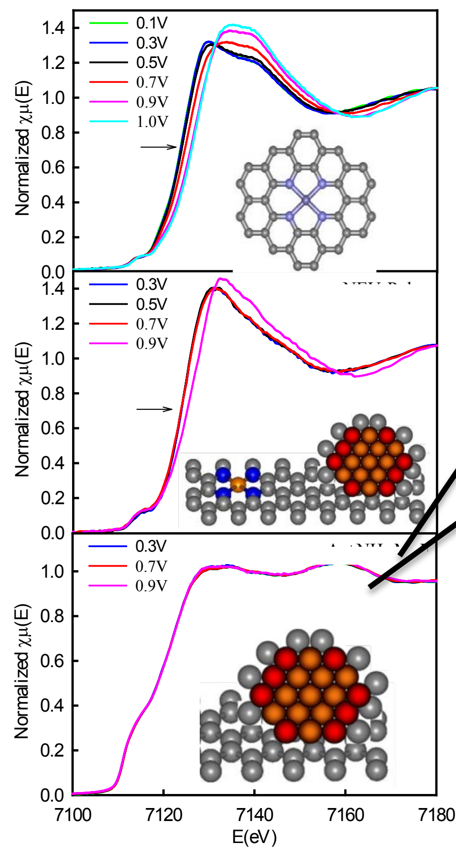


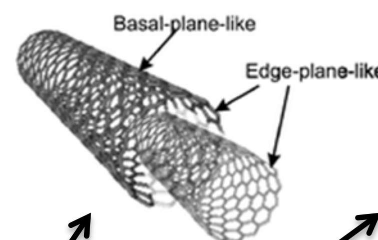
- **Key process steps and variables established and being adjusted for x20 scale**
- **Promising performance of initial x10 batches established**

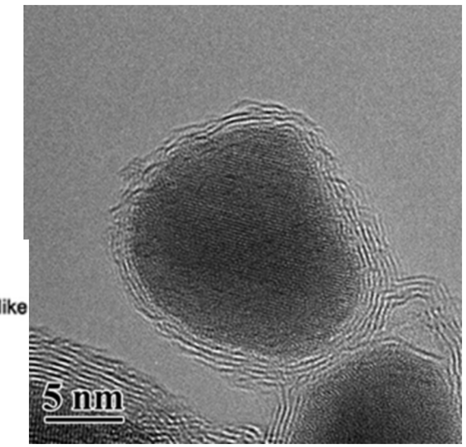
Two major active sites identified by *in situ* XAS











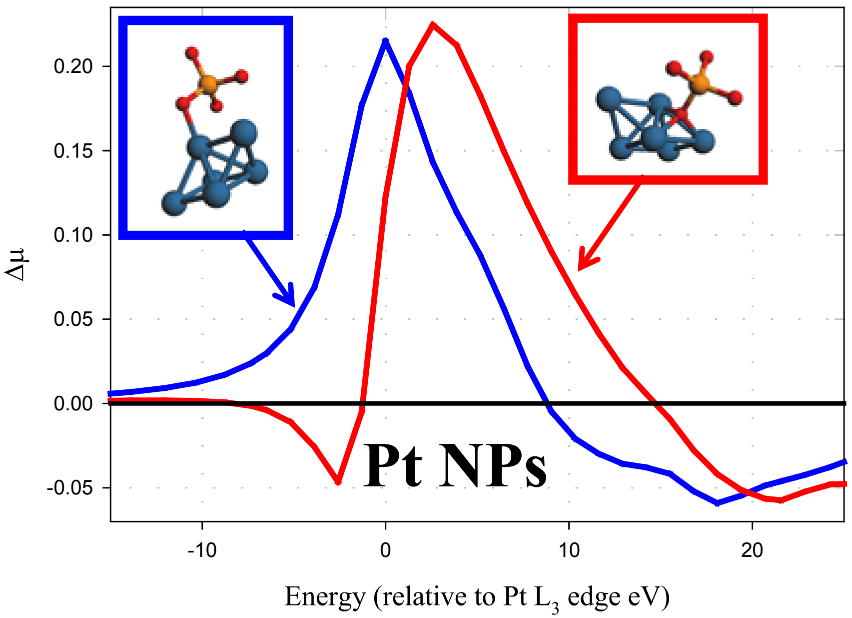
The two major types of active sites in heat-treated Fe-N-C catalysts can be clearly distinguished by *in situ* XAS.

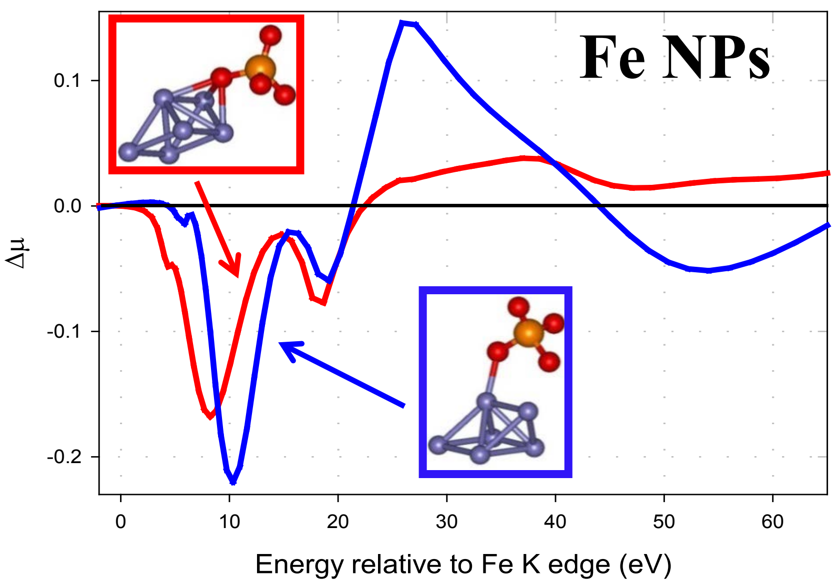
The local geometry, and relative content of each site can be quantitatively determined by EXAFS fitting.

This information facilitates to have controls over the content of the catalysts by controlling the precursors and the preparation procedures.

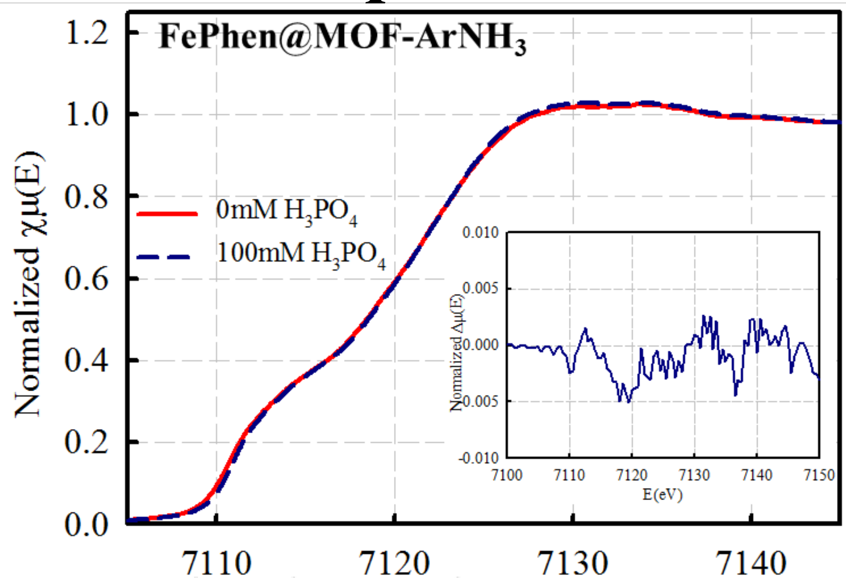
Anion Adsorption

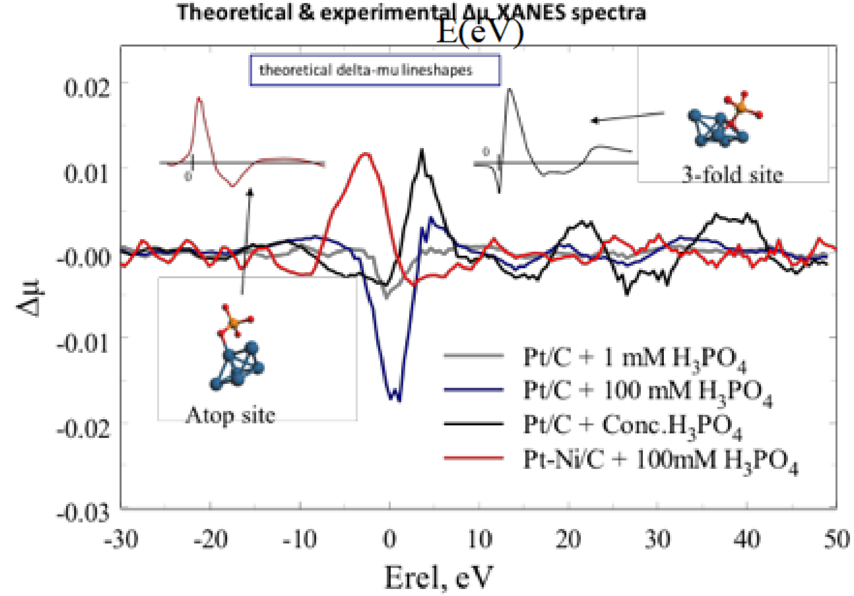
Theoretical





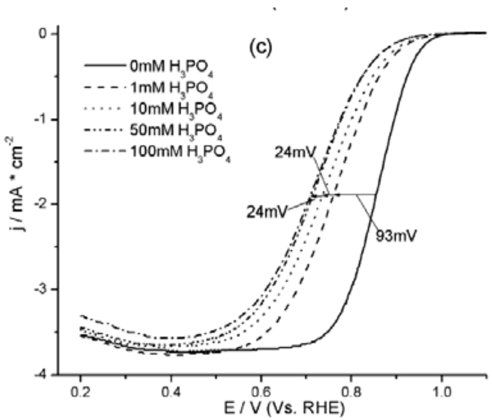
Experimental

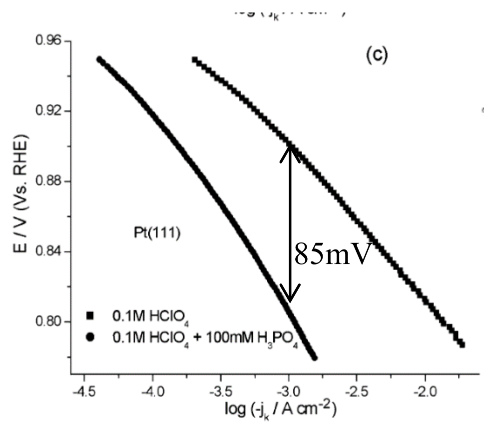




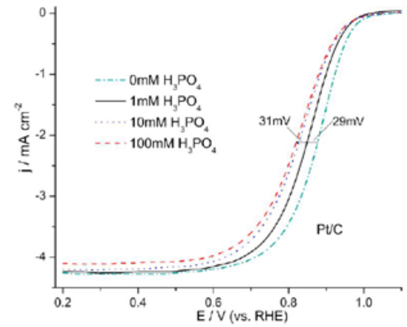
Q1 - RDE Phosphate Poisoning & Inter-Intra Batch Variability

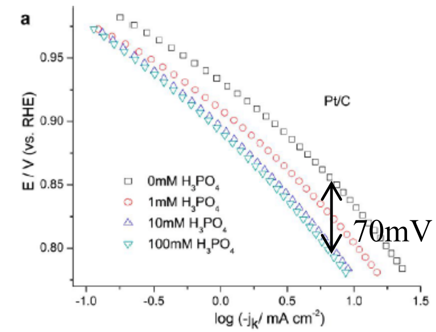
Pt (111)
Qinggang He et al, Physical Chemistry Chemical Physics 2010



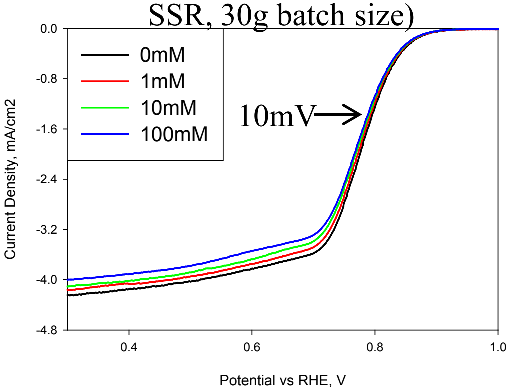


Pt/C
Qinggang He et al, Journal of Physical Chemistry C, 2013

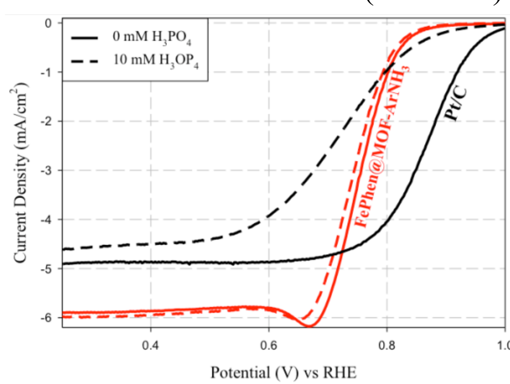


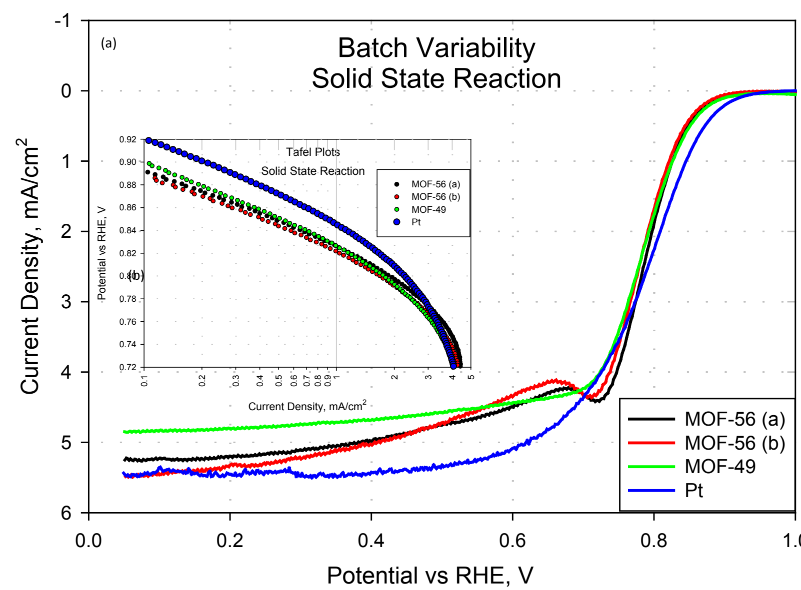


MOF Solid State Reaction (MOF-SSR, 30g batch size)



MOF Solution Reaction (MOF-SR)





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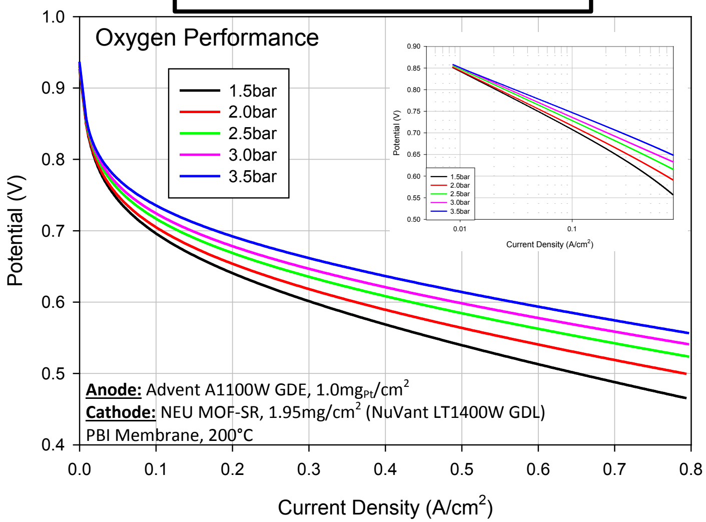
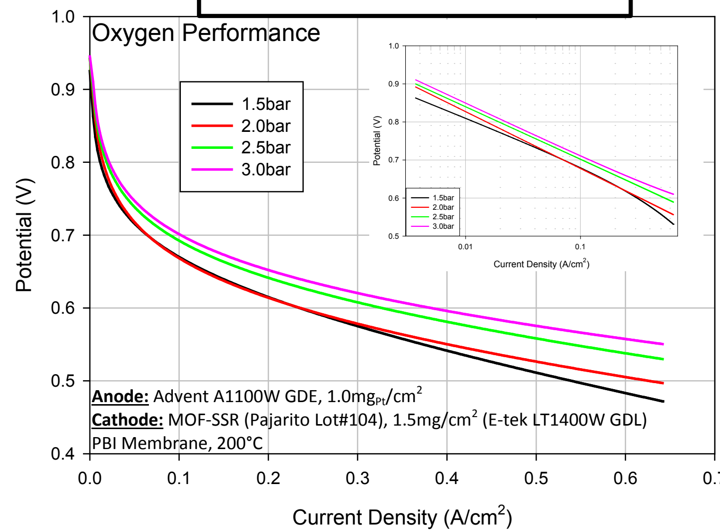
Q2/Q3/Q4 - Measurements in a Phosphoric Acid Fuel Cell Interface – MOF Approach

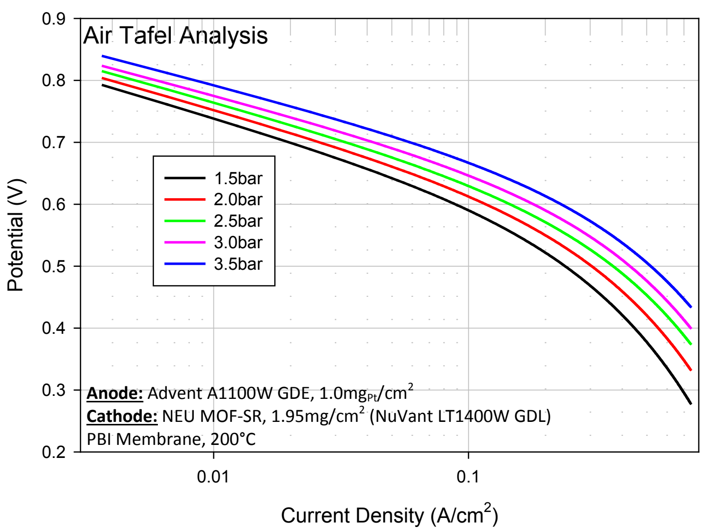
H_2/O_2 & H_2/air, 200˚C, PBI Membrane

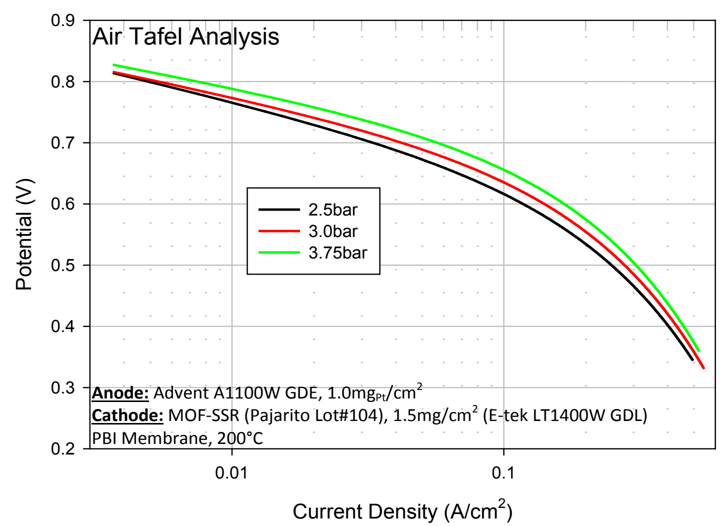
MOF Solution Reaction



MOF Solid State Reaction







Fe-N-C ORR Catalyst in PBI MEA

MEA Polarization – Back Pressure Effects @ 180 C

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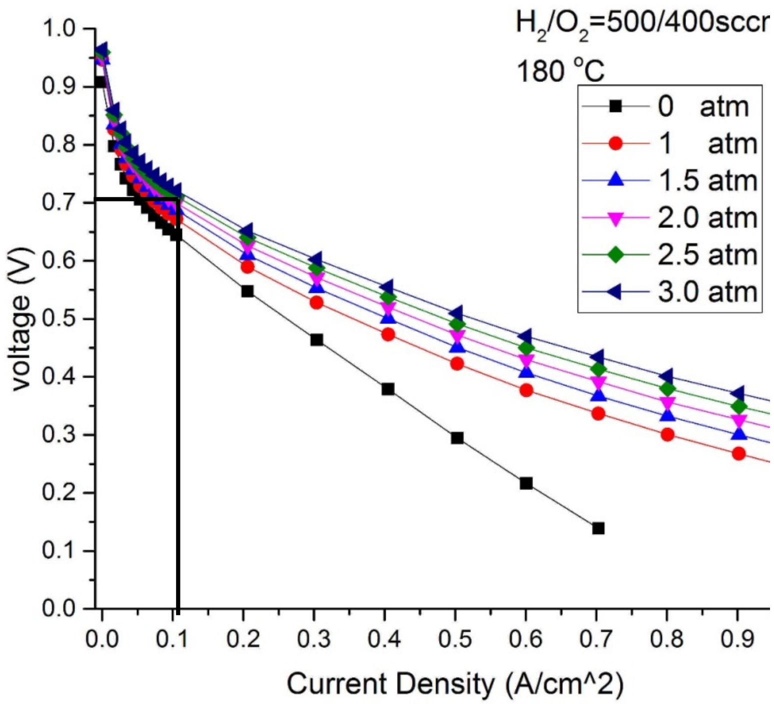
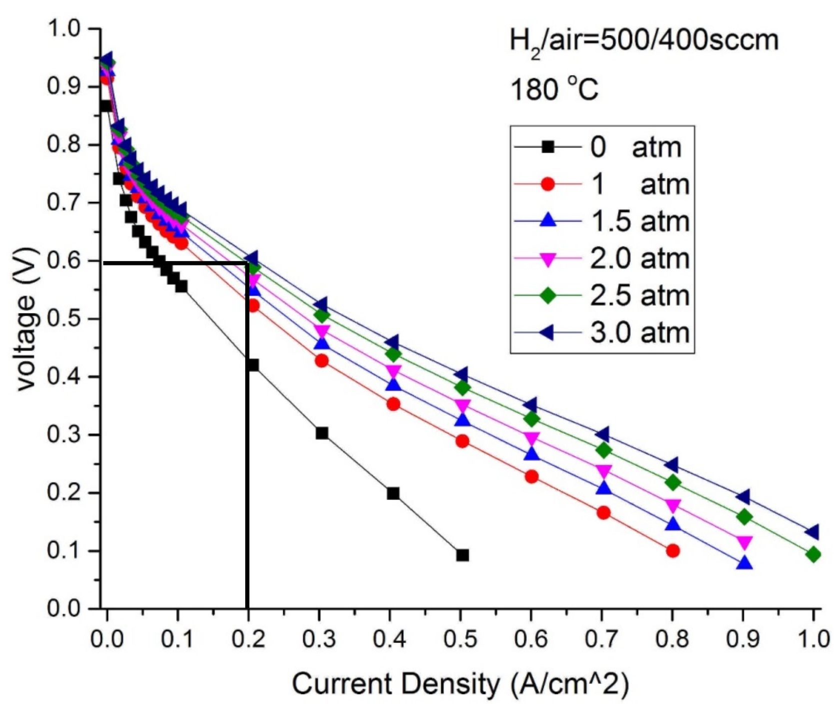
GO/NO-GO DECISION





β-site testing: **Brian Benicewicz**

UNIVERSITY OF SOUTH CAROLINA

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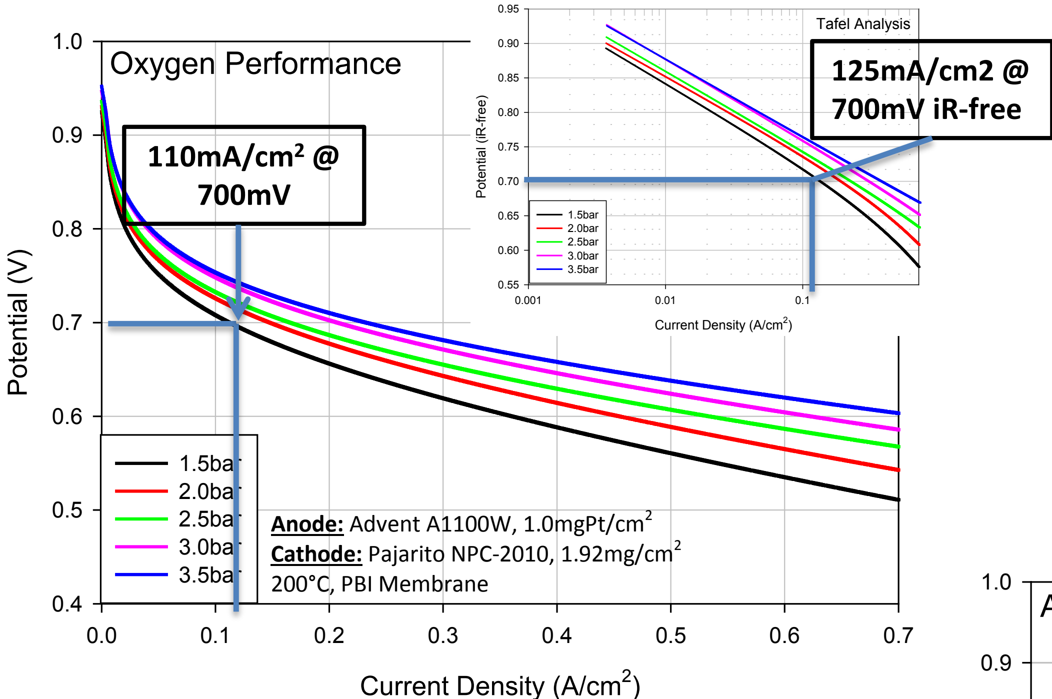
NPC-2010 (Pajarito) – Best Data To Date – (Tested at NEU)



O_2, 1.5bar:

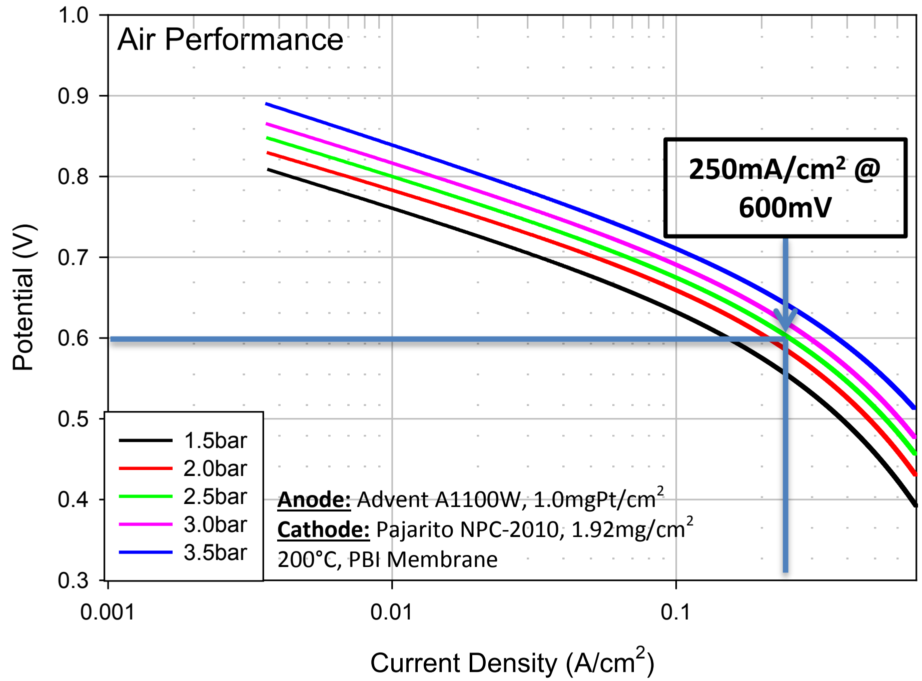
- $110 mA/cm^2$ @ 700mV (raw)
- $125 mA/cm^2$ @ 700mV (iR-free)

Air, 2.5bar:

- $250 mA/cm^2$ @ 600mV
- $200 mA/cm^2$ @ 620mV

NPC-2010 testing done at 200°C for both performance at durability.

- Elevated temperature should be more taxing during durability, so performance was done at same temperature for consistency.



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PAJARITO POWDER

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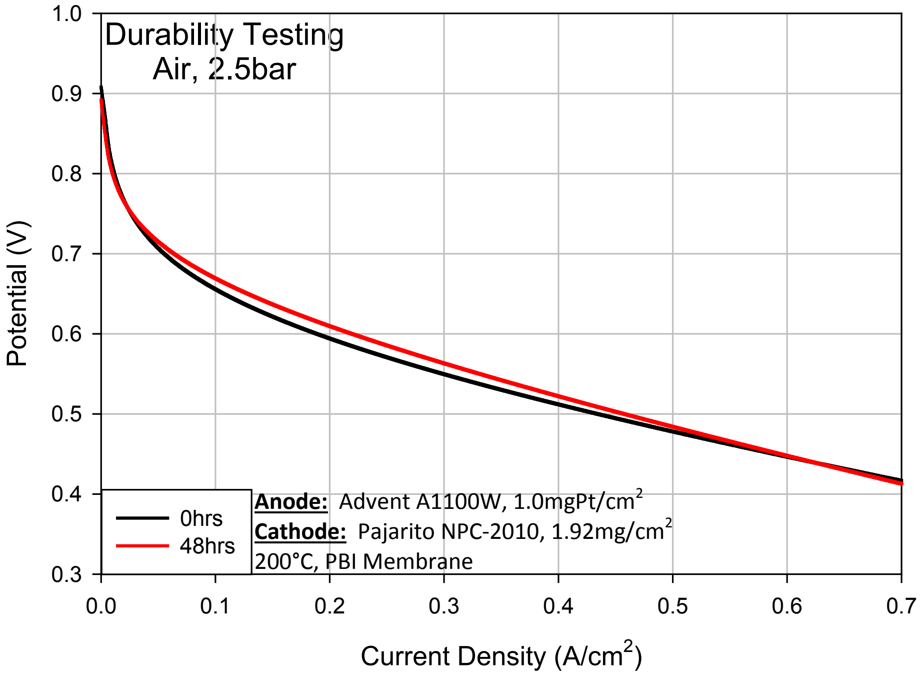
Q5/Q6 - Durability in a Phosphoric Acid Fuel Cell Interface (Tested at NEU)

H_2/air, 200˚C, 2.5 bar total pressure, PBI Membrane



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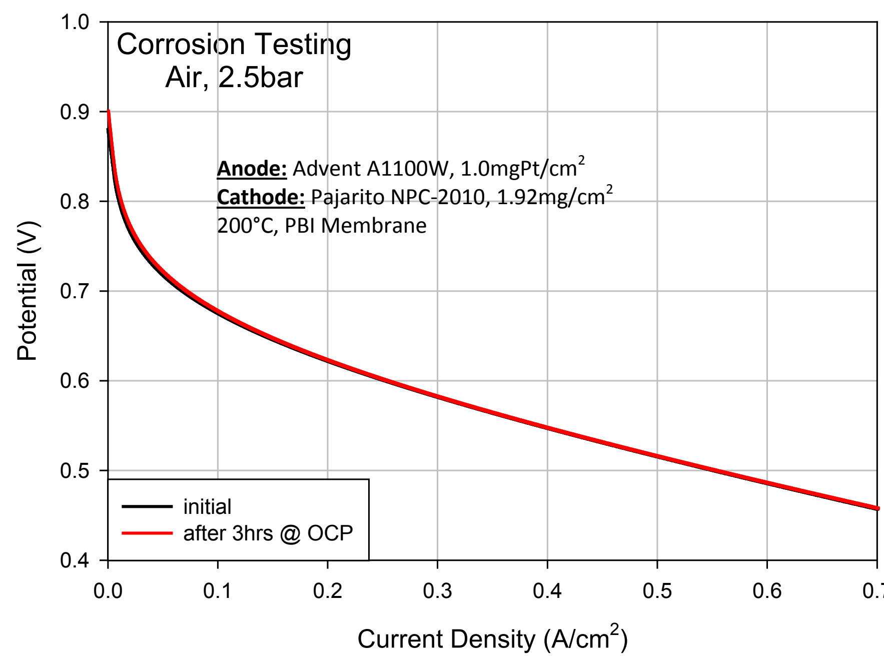
PAJARITO POWDER

Pajarito NPC-2010 Catalyst:
- 1.92mg/cm²



Chronopotentiometric Testing (Q5, top):
- No performance losses after 48hrs

Corrosion Testing (Q6, right):
- No change in performance after 3hr hold @ OCP

Summary

- Q1: RRDE demonstrating Non-PGM with phosphate immunity
  - **Status:** Target **ACHIEVED**, as both MOF-SR and MOF-SSR demonstrate high immunity towards phosphate poisoning
- Q2: Fuel cell performance demonstrating 100mA/cm^2 (iR-free) at 700mV in H_2/O_2, 1.5bar total pressure (7psig)
  - **Status:** Target **ACHIEVED** with MOF-SR and MOF-SSR tested at NEU as well as UNM catalyst tested at USC
- Q3 & Go/No-Go: Fuel cell performance demonstrating 200mA/cm^2 at 600mV in H_2/air, 2.5bar total pressure (21psig)
  - **Status:** Target **ACHIEVED** with UNM catalyst tested at USC. At elevated temperature (200°C),target **ACHIEVED** with Pajarito NPC-2010 tested at NEU. MOF-SR and MOF-SSR tested at NEU are 20 & 50mV shy of target, respectively. Other UNM & Pajarito materials testing in progress at NEU.
- Q5 (April 1 – June 30, 2017): Chronopotentiometric testing at 800mV (H_2/air, 2.5bar), less than 5% losses through 24-48 hours at 650mV
  - **Status:** Target **ACHIEVED** with Pajarito NPC-2010, while maintaining Go/No-Go performance metric, even at elevated temperature. Testing in progress with other Non-PGMs at NEU.
- Q6 (April 1 – June 30, 2017): Corrosion Resistance demonstrating less than 3% losses at 650mV (3hr hold at OCP, H_2/air, 2.5bar)
  - **Status:** Target **ACHIEVED** with Pajarito NPC-2010, while maintaining Go/No-Go performance metric. Testing in progress with other Non-PGMs at NEU.

Ongoing and Future Efforts

- Continued Development of Non-PGMs at UNM & Pajarito
  - In order to achieve Q7 target (catalyst down-select)
    - 200mA/cm^2 at 650mV (H_2/air, 2.5bar)
- Continued Durability testing at NEU
  - Chronopotentiometric testing (24-48hrs) at NEU (Q5)
    - Pajarito NPC-2010 demonstrated durability over 48hrs while exceeding Go/No-Go performance metric. Anticipate similar durability from other Non-PGM materials.
  - Corrosion Resistance testing at NEU (Q6)
    - Pajarito NPC-2010 demonstrated no performance losses while exceeding Go/No-Go performance metric. Anticipate similar durability from other Non-PGM materials.
  - Temperature cycling durability from 90-200C (50 cycles)
- MEA Scale up (Q8)
  - New commercial test stations will allow for NEU to do both longer term testing as well as larger MEAs
    - Through partnership with Advent, NEU is currently capable of fabricating and testing 45cm^2
      - Based on performance of 45cm^2 vs 5cm^2, NEU will look at possibility of expanding to 100cm^2.
        - » Would require both new fabrication tools as well as cell hardware for that expansion.

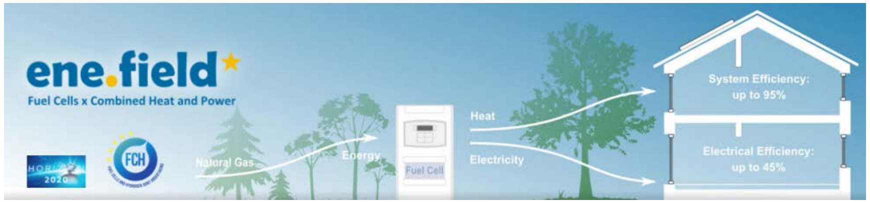
Any proposed future work is subject to change based on funding levels

Technology to Market

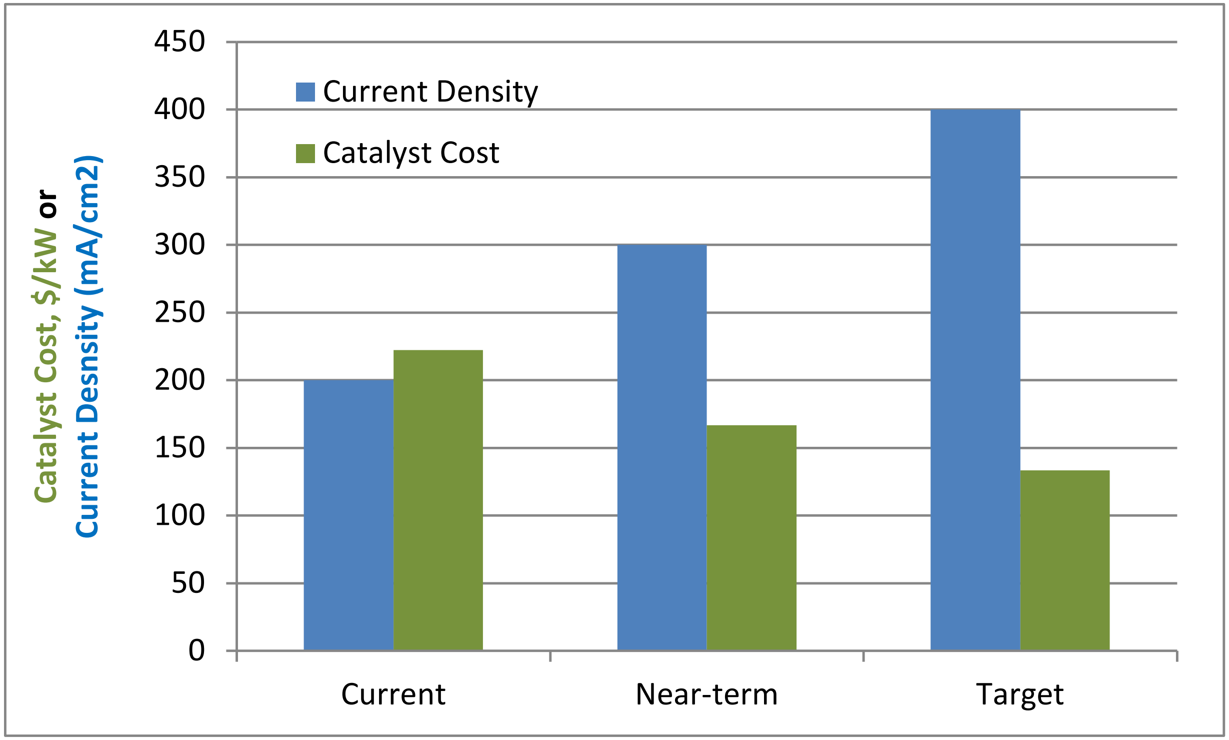
- ***Benefits of High-temperature PEMFC with PGM-free catalyst***
  - Opportunity fuels: lower cost reformates and waste hydrogen streams in industrial market (10,000 – 30,000 ppm CO tolerance)
  - H_2 clean-up equipment reduction by 80-90% → simpler, more robust system, lower cost
  - Smaller radiator
  - Additional revenue from by-product heat/steam
- ***PGM-free Catalyst Manufacturing***
  - Pajarito Powder has scaled up non-PGM catalyst fabrication, test marketing in progress
  - Target markets
    - Stationary power (including CHP)
    - Backup power
    - Material handling
- ***Linking FC Technology to Natural Gas Economy***
  - Flare gas associated with oil and coal production (>10,000 MW potential)
  - Barrier to widespread deployment: CAPEX (~$20k) too high; need <$10k

Lessons Learned

- Early examples of micro-CHP units - high CapEx and OpEx:
  - UTC TARGET program (1970+): 4 kW PAFC (CO-tolerant)
    - Consortium of 32 gas or mixed gas-electricity companies
  - PlugPower/GE, ClearEdge (2000+): 5 kW PEM systems
    - Deployed >1000 systems, natural gas fuel
- Japan: ene-farm has deployed >200,000 units
- Europe: ene.field has a goal of 1,000 CHP units in 11 countries



Use of PGM-free Cathode Catalyst



Reduced price fluctuations associated with Pt

- Potential for 50% cost reduction via PGM-free supply chain
- Use of lower cost hydrogen streams as fuel
- Use of Flare gas – new market opportunity
- CHP benefits

Collaborations

Partners (this project)

- Northeastern Univ., (Prime) Boston, MA: S. Mukerjee (P.I)
- The Univ. of New Mexico, Albuquerque, NM: P. Atanassov (Univ., sub-contractor)
- Pajarito Powder, LLC, Albuquerque, NM: B. Zulevi (Industry, sub-contractor)
- Advent Technologies, Inc., Cambridge, MA: E. De Castro (Industry, special materials supplier)
- eT2M, Danbury, CT: L. Lipp (Industry, T2M research vendor)

Other collaborators:

Jean-Pol Dodelet, Pajarito Powder LLV (Scientific Board Member)

Frederic Jaouen, University of Montpelier (France)

Brian Benicewicz, University of South Carolina

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.