Innovative Non-PGM Catalysts for High-Temperature PEMFCs

2016 DOE Hydrogen and Fuel Cell Program Review

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Project ID# FC132

Overview Project [DE-EE0006965]

- **Timeline**:
  - Start date: 7/01/2015
  - End date: 8/31/2017
- **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 PGM/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 compared to perfluorinated proton conducting membrane.
  - **Activity Targets**: for Non-PGM 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, Non-pgm 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 University*, (*Prime*) Boston, MA: S. Mukerjee (P.I)
  - *The University of New Mexico*, (*Sub-awardee*) Albuquerque, NM: Prof. P. Atanassov (Co-P.I)
  - *Pajarito Powder, LLC*, (*Sub-awardee*) Albuquerque, NM: Dr. B. Halevi (Co-P.I)
  - *Fuel Cell Energy, Inc.* (*Sub-awardee*) Danbury, CT: Dr. L. Lipp (Co-P.I)
  - *Advent Technologies, Inc.* (*special materials supplier/vendor*): Cambridge, MA: Dr. E. De Castro

Relevance

- Objectives: To investigate the use and development of non-PGM electrocatalysts that would allow for high performance in high-temperature proton exchange membrane fuel cells. The performance targets that should be met and exceeded are 100mA/cm^2 @ 700mV (H_2/O_2. 1.5bar total pressure) & 200mA/cm^2 @ 600mV (H_2/air, 2.5bar total pressure).
- Relevance to DOE Mission: This will enable HT-PEM technology to be less dependant on Pt resource availability and lower MEA costs by at least 50%.
  - Significant changes in energy efficiency, carbon footprint, and United States energy security
- Impact
  - Current high Pt loading costs $750-1000/KW
  - 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.

Overall Approach

- **Overall technical approach:**
  - **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) using 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
- **Program Technical Barriers and Approach to Overcome them:**
  - 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
    - (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

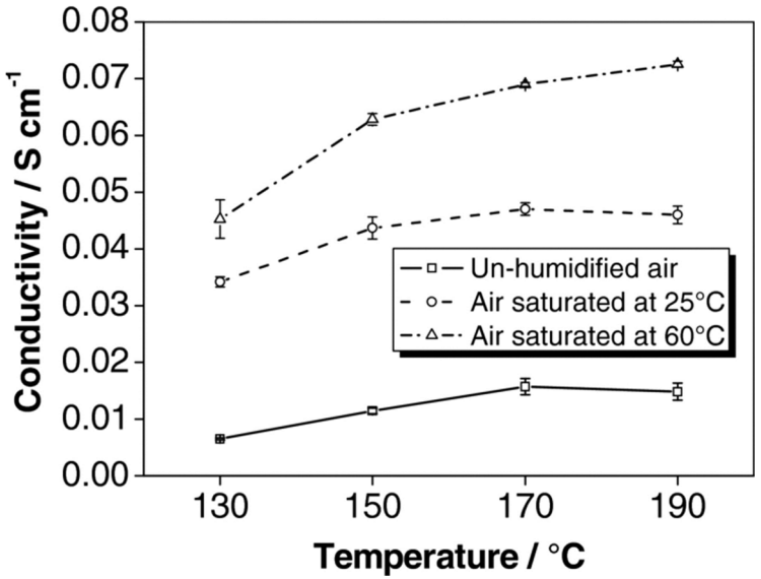
Key Barriers and Motivation

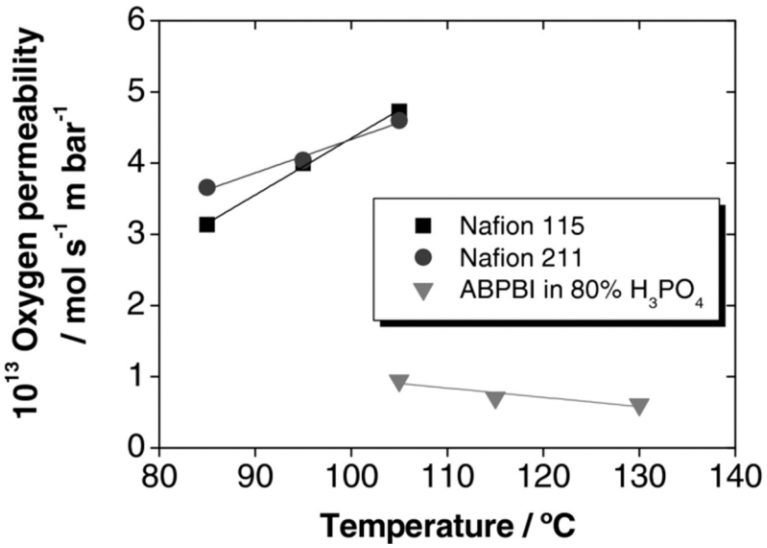
- Successfully commercialized for stationary power applications
- 10 year stack life and 20 year product life
- Operates at ~ 150-200°C
- 81% total CHP efficiency
- 90-100% Phosphoric Acid electrolyte
  - Durable Membranes Available
- Pt-based catalyst for anode and cathode Key Barrier

Cost and Performance Characteristics[10]	System 1	System 2	System 3	System 4	System 5	System 6
Fuel Cell Type	PAFC	PEM	PEM	MCFC	MCFC	SOFC
Nominal Electricity Capacity (kW)	200	10	200	300	1200	125
Commercial Status 2007[11]	Com'l	Com'l	Demo	Com'l	Com'l	Demo
Operating Temperature (° F)	400	150	150	1200	1200	1750
Package Cost (2007 $/kW) [12]	4,500	8,000	n.a.	4,000	3,870	n.a.
Total Installed Cost (2007 $/kW) [13]	6,310	9,100	n.a.	5,580	5,250	n.a.
O&M Costs (2007 $/kW) [14]	0.038	n.a.	n.a.	0.035	0.032	n.a.
Electric Heat Rate (Btu/kWh)[15]	9,480	11,370	9,750	8,022	8,022	8,024
Electrical Efficiency (percent HHV)[16]	33%	30%	35%	43%	43%	43%
Fuel Input (MMBtu/hr)	1.9	0.1	2	2.4	9.6	1.00
CHP Characteristics						
Heat Avail. >160° F (MMBtu/hr)	0.375	0	0	n.a.	n.a.	n.a.
Heat Avail. <160° F (MMBtu/hr)	0.475	0.04	0.72	0.48	1.9	0.34
Heat Output (MMBtu/hr)	0.850	0.04	0.72	0.48	1.90	0.34
Heat Output (kW equivalent)	249.0	11.7	211.0	140.6	556.7	100.0
Total CHP Efficiency (percent), HHV[17]	81%	65%	72%	62%	62%	77%
Power/Heat Ratio[18]	0.80	0.85	0.95	2.13	2.16	1.25
Net Heat Rate (Btu/kWh)[19]	4,168	6,370	5,250	6,022	6,043	4,611
Effective Electrical Eff (percent), HHV	81.90%	53.58%	65.01%	56.67%	56.48%	74.02%

Source: EEA/ICF

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





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

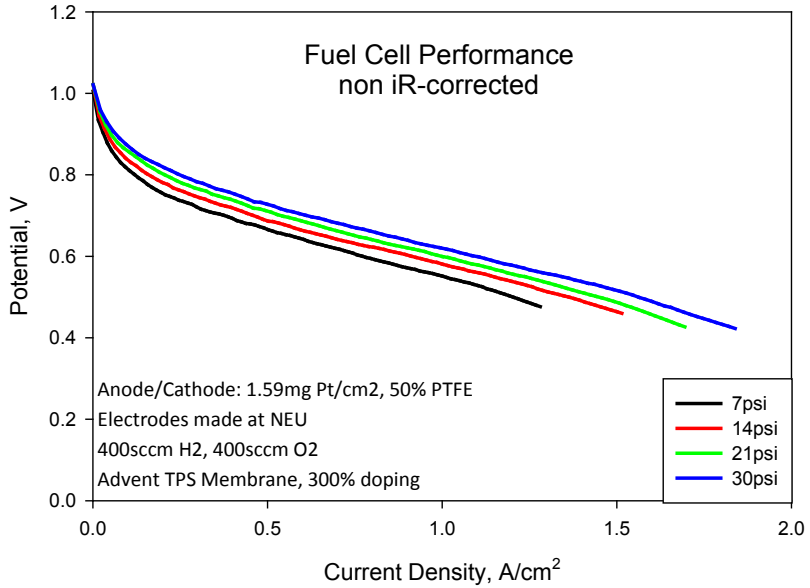
*Nafion Membrane: 100% humidified

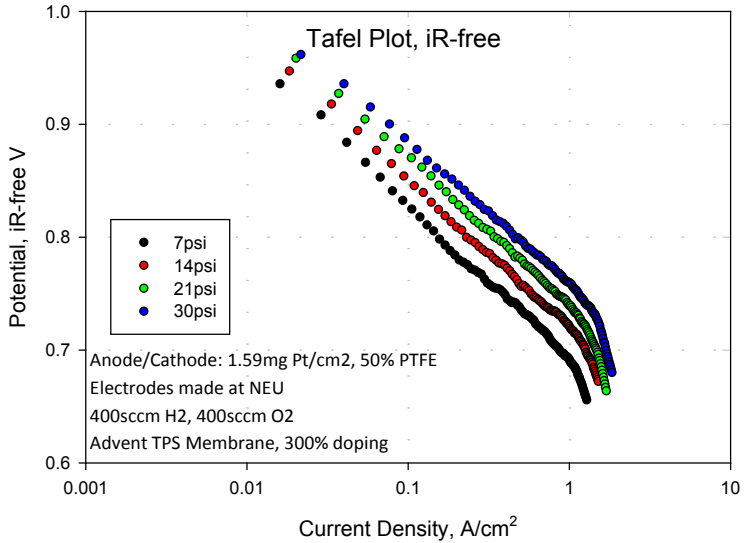
Balance of Plant
CO Tolerance: < 2% above 160°C
S Tolerance: 100 ppm
No need for Prox unit

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

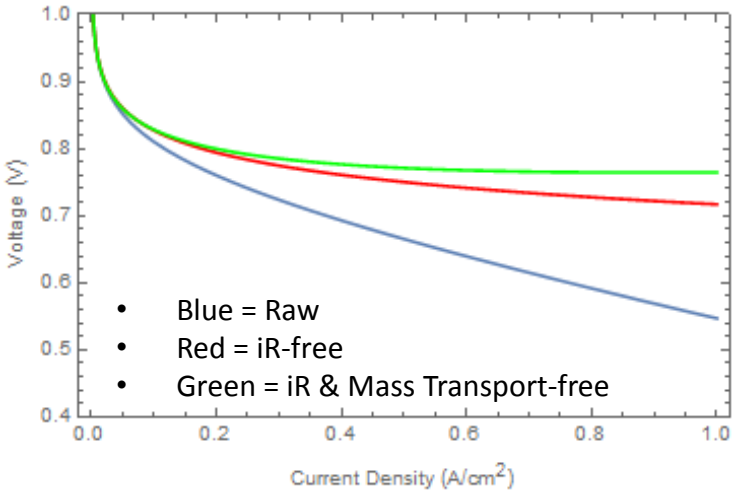
Pt Reference Data with Advent TPS Membrane

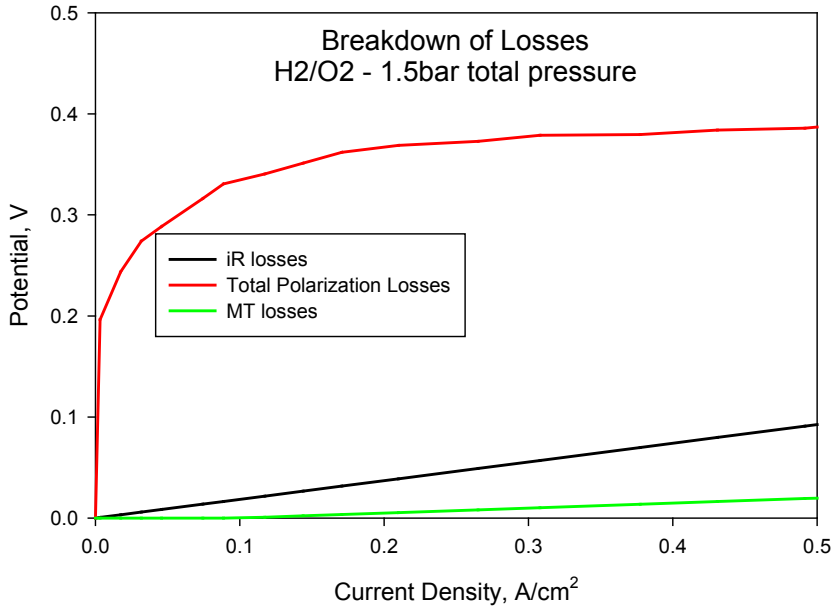
Backpressure-dependent Performance, O_2



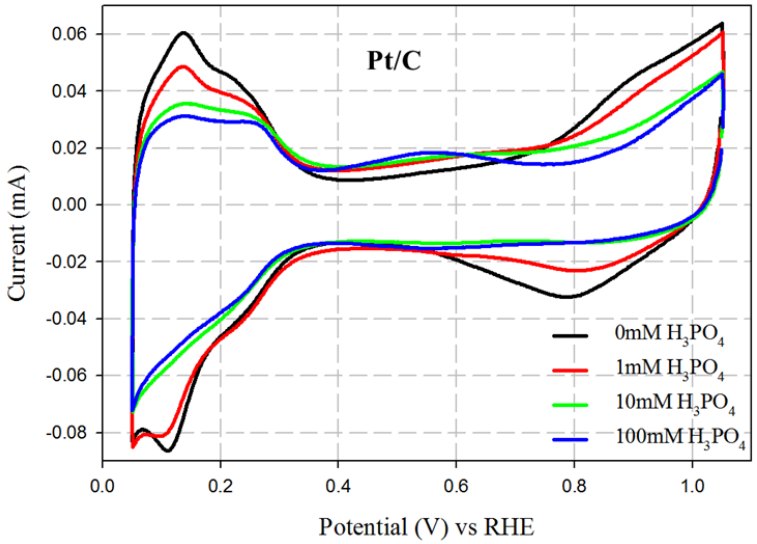


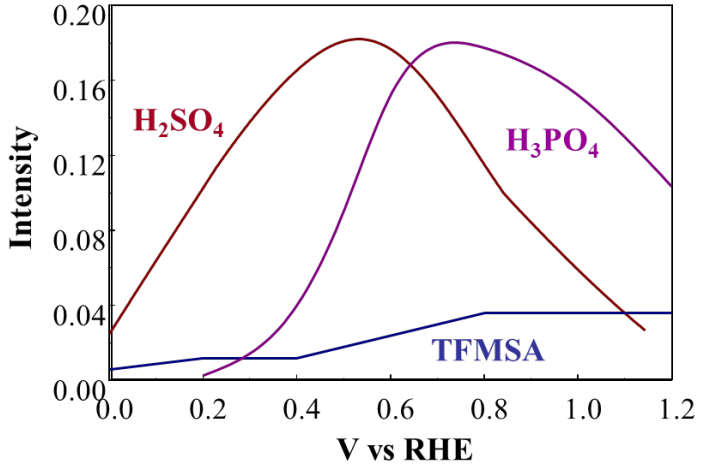
H_2 / O_2 Overpotential analysis at 180°V & 1.5bar total pressure



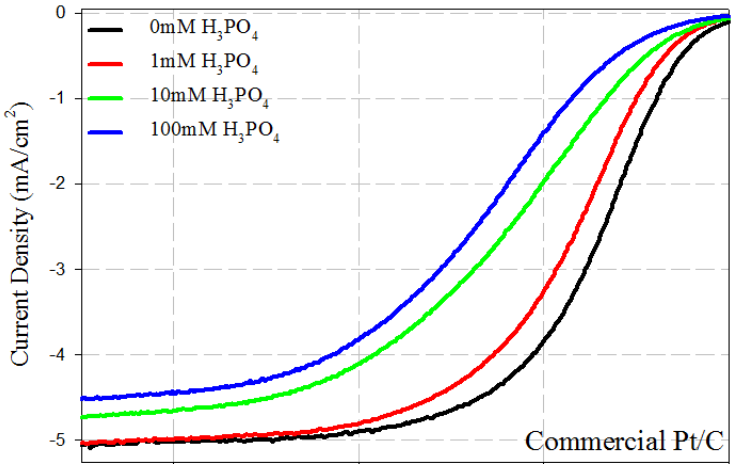


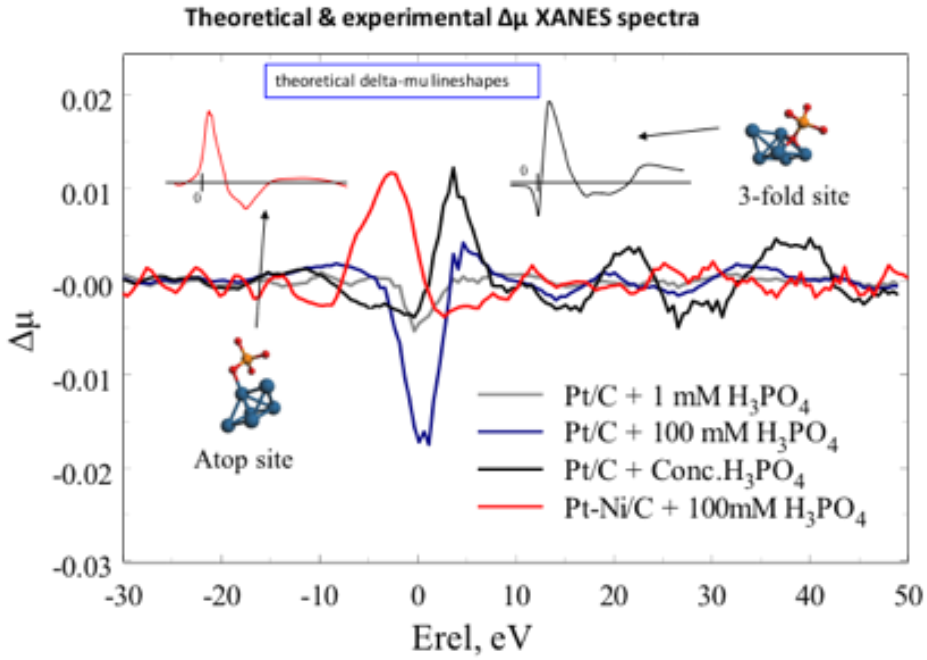
Phosphate Anion





Zolfaghari et al *J. Electrochem. Soc.* **144** (1997) 3034-3040

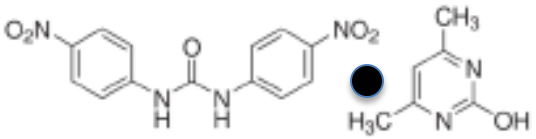




Development of Novel MNC Catalysts

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

❖ **Mechano-Chemical Approach (UNM)**



Nicarbazin

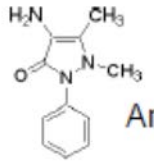
Ball milling

+ Fe-Salt+ Silica templated

UNM-CTS

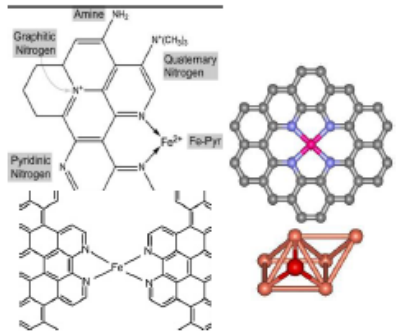
Pyrolysis

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



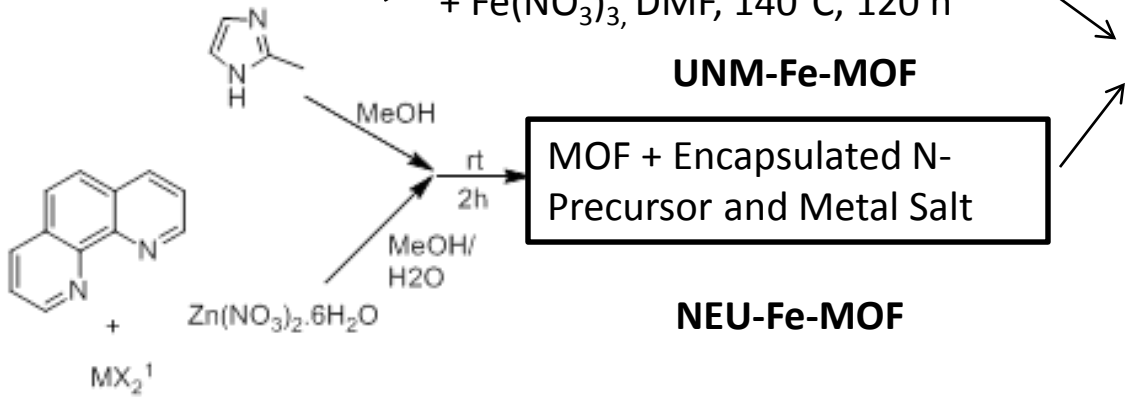
Aminoantipyrine

+ Fe-Salt+ Silica templated



M-N-C catalyst

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

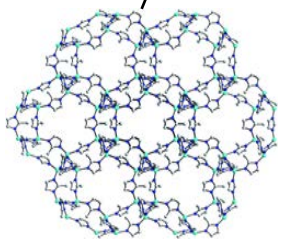


+ $Fe(NO_3)_3$, DMF, 140°C, 120 h

UNM-Fe-MOF

MOF + Encapsulated N-Precursor and Metal Salt

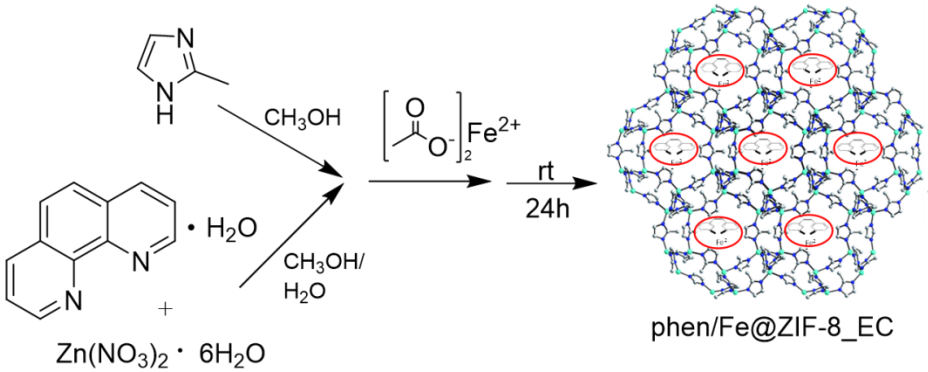
NEU-Fe-MOF

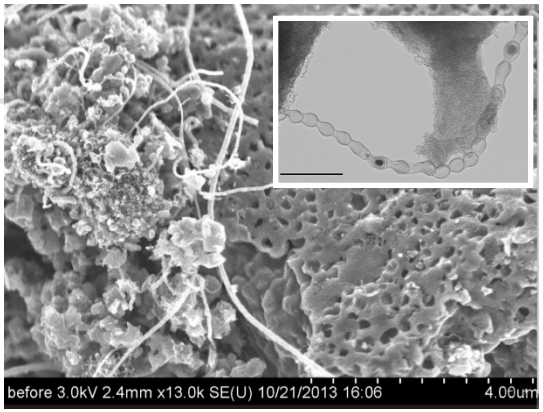


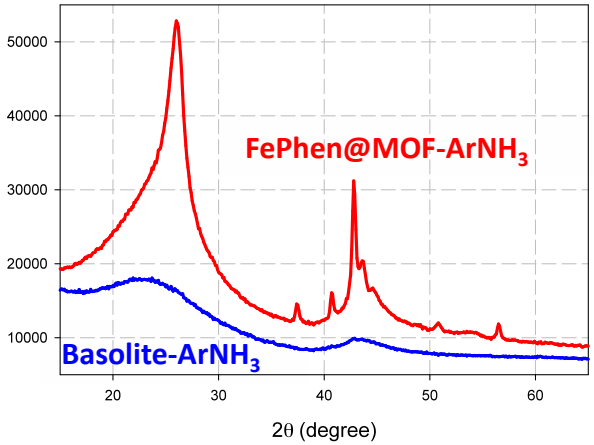
[1] M=Fe, Co; X=$C_2H_3O_2$, Cl

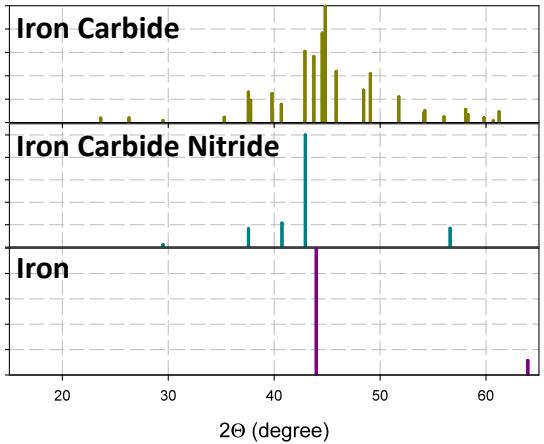
[2] '@' indicates chemical encapsulation of phenanthroline and metal (M-N_4 active site)

Metal Salt Encapsulation

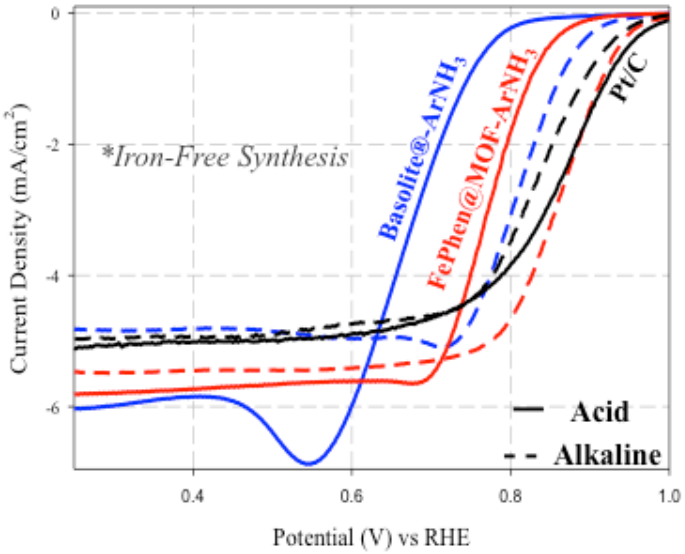


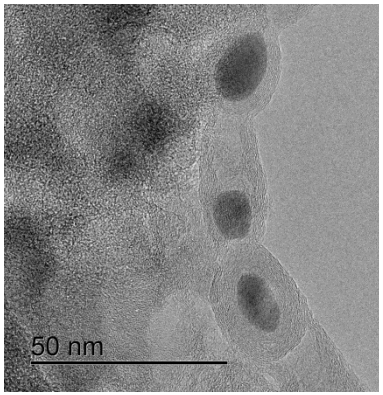


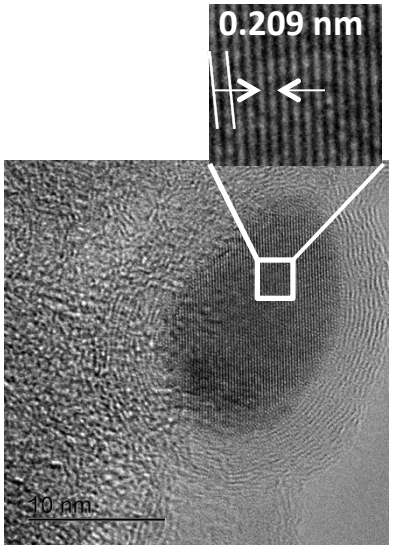




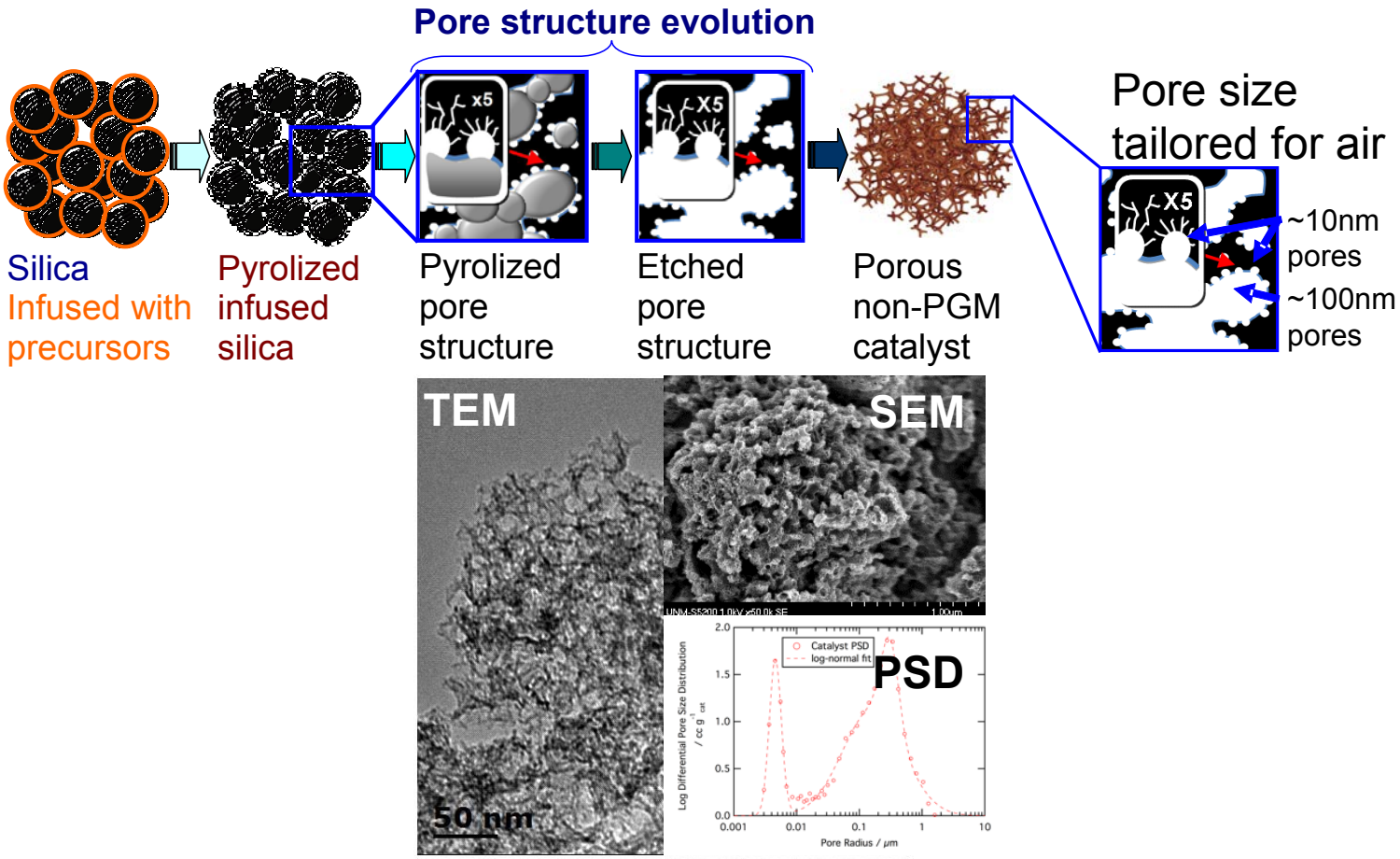
FePhen@MOF-SR







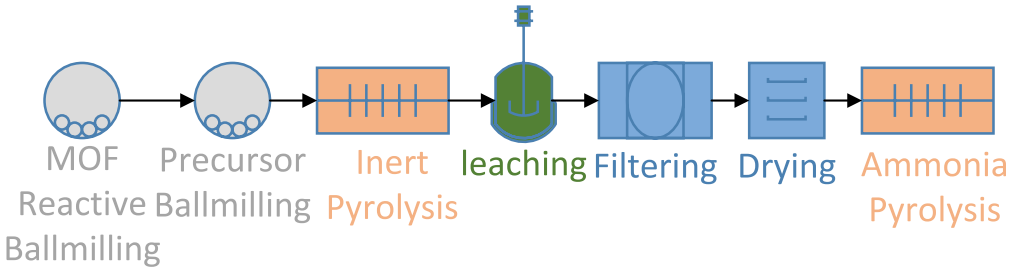
Fe-CTS Modification for Air and Scale Up

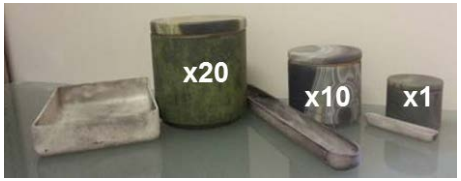


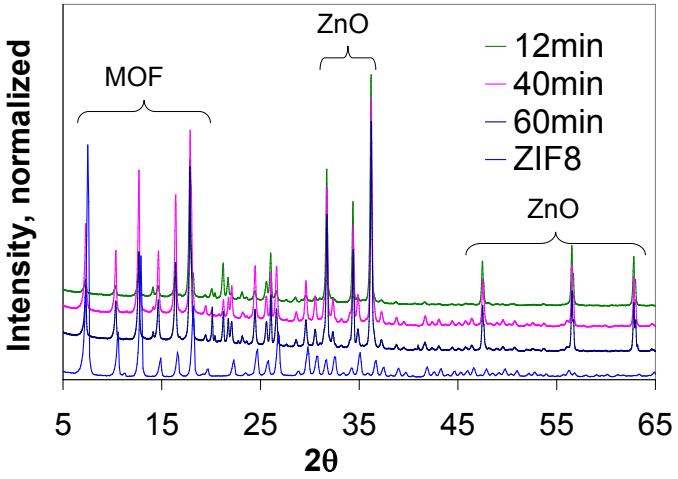
- **UNM SSM method Fe-CTS catalyst porosity modified for air operations and scaled to 200gram per batch**

Fe-MOF tech Transfer and Scale Up

Reactive Milled MOF processing established



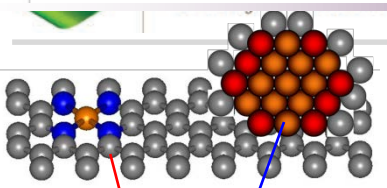


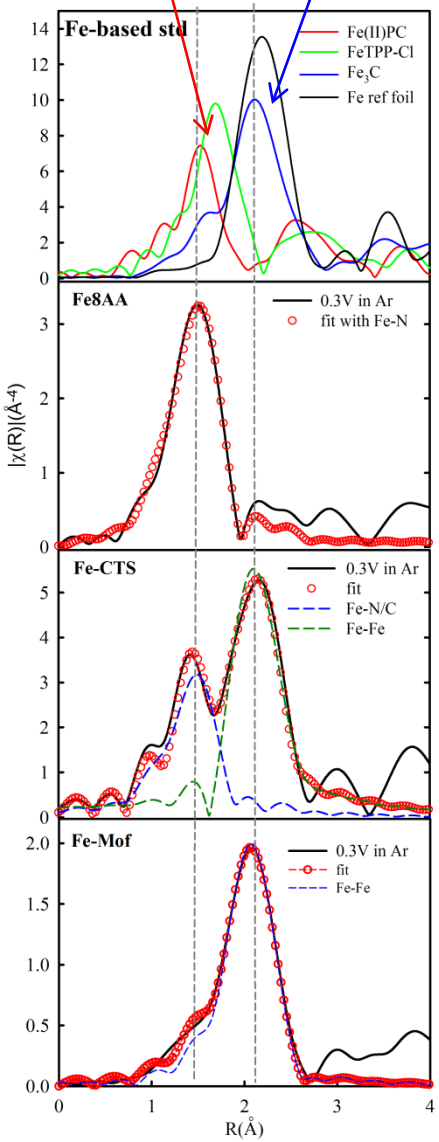


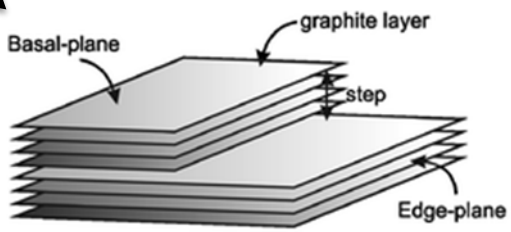
- **Key process steps and variables established and being adjusted for x20 scale**
- **Promising performance of initial x10 batches established**

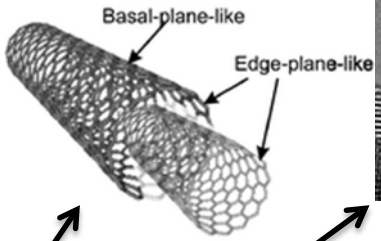
In Situ XAS Studies at the Fe K edge

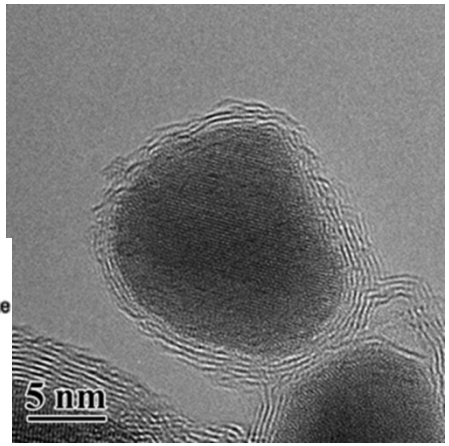
Two major active sites identified by *in situ* XAS

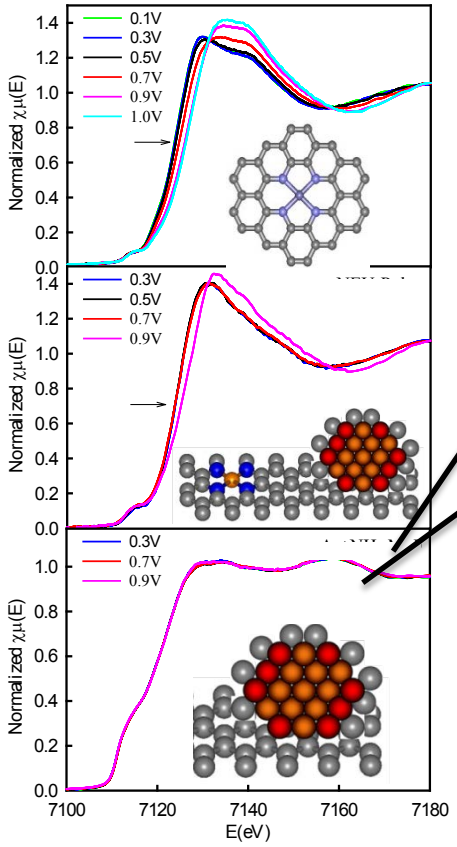












The two major types of active sites in heat-treated Fe-N-C catalysts can be clearly distinguished by *in situ* XAS.

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

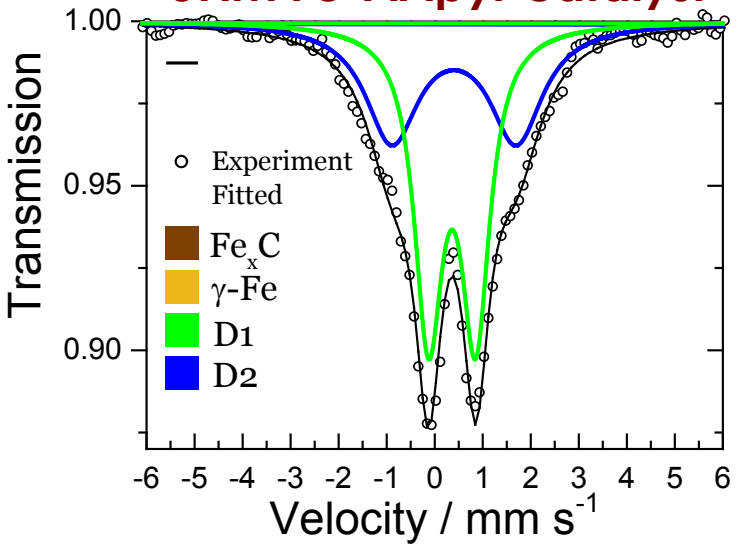
This information facilitates to have controls over the content of the catalysts by controlling the precursors and the preparation procedures.

^{57}Fe Mössbauer Spectroscopy

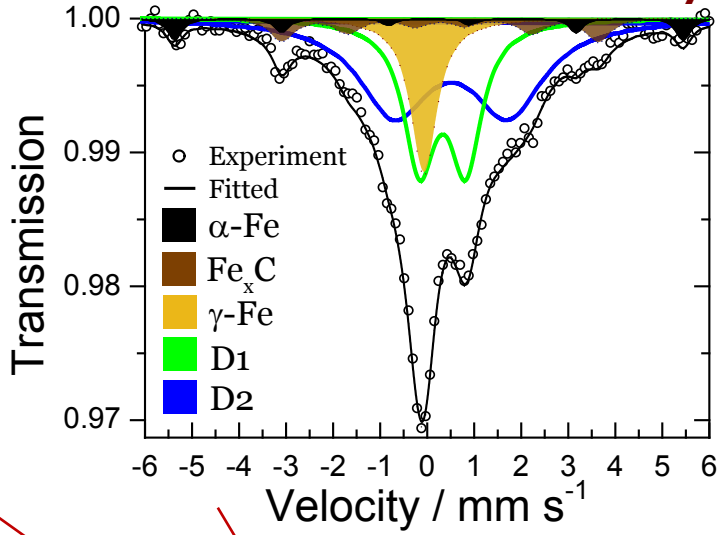
Frederic Jaouen

Spectroscopic observations of the chemical moieties

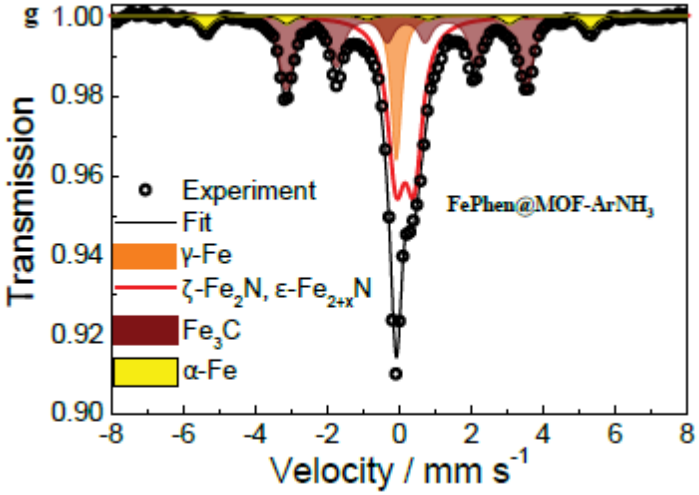
UNM Fe-AApyr catalyst

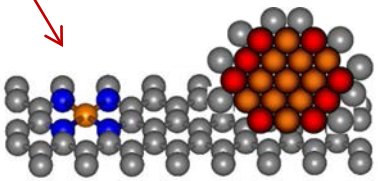


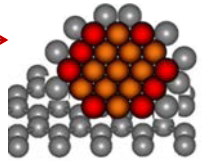
UNM Fe-Nicarbazin catalyst

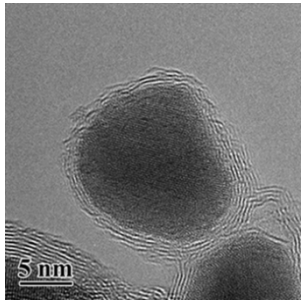


NEU-MOF



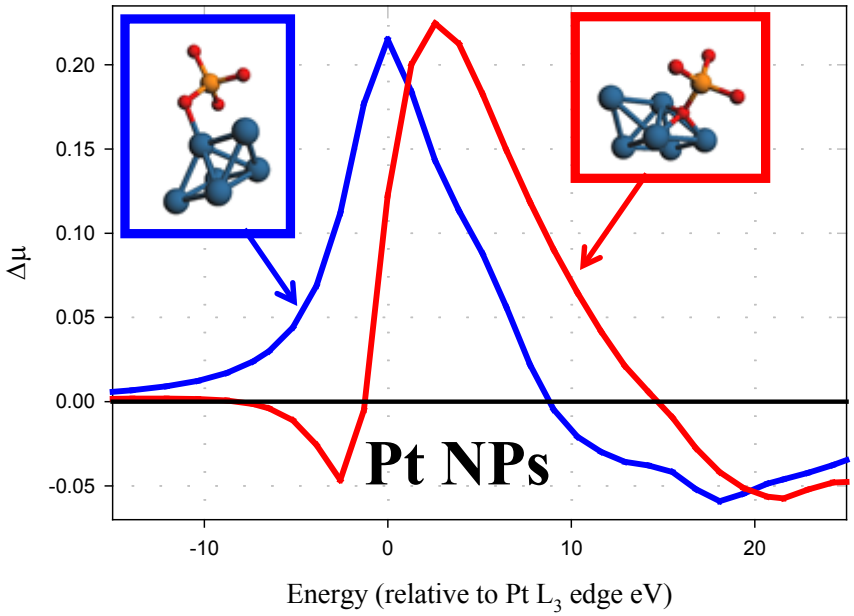


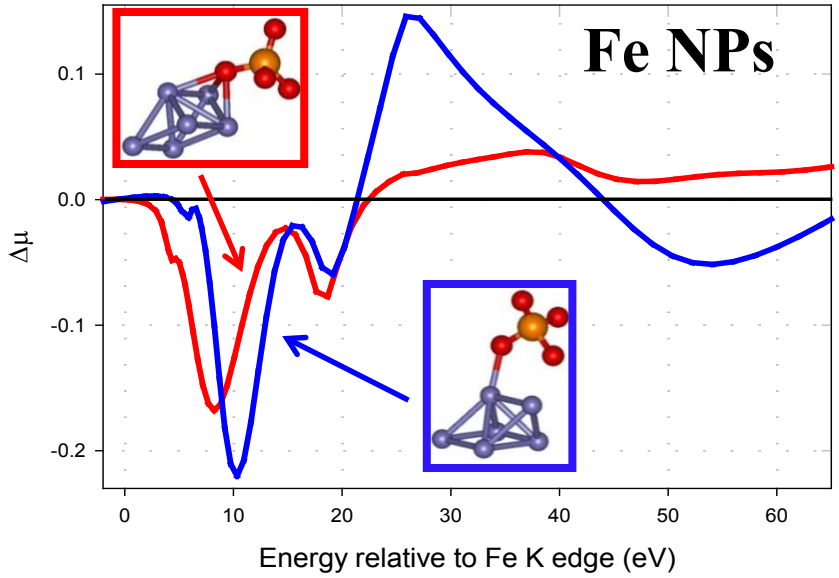




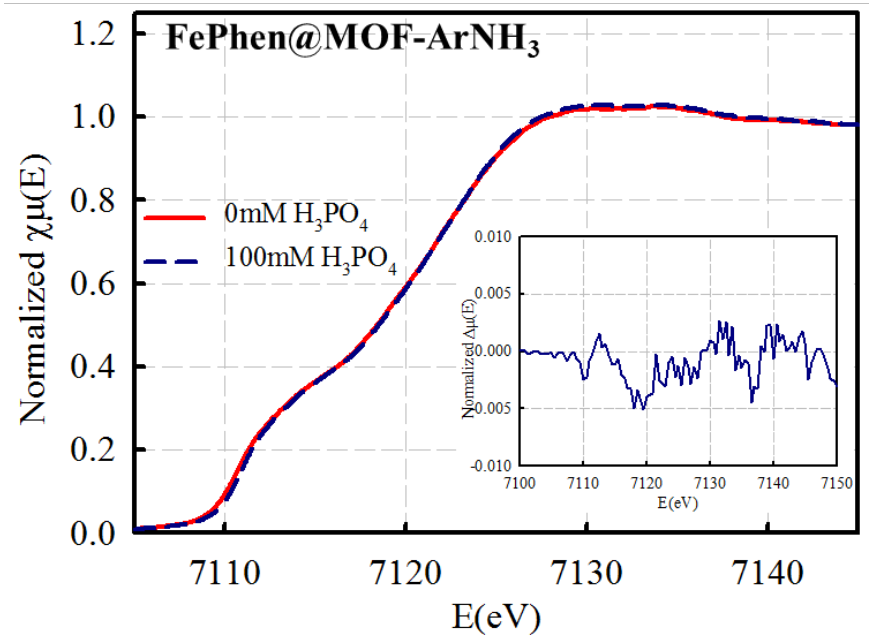
Anion Adsorption

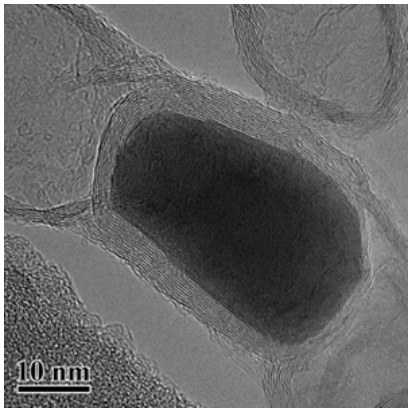
Theoretical





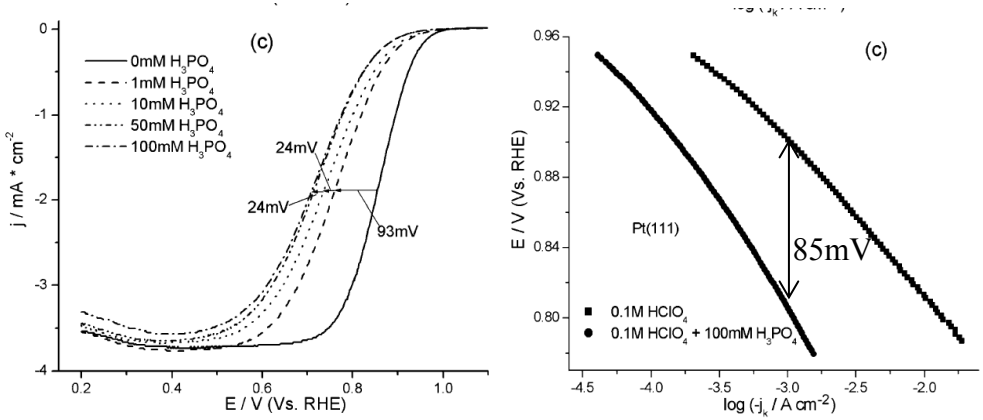
Experimental



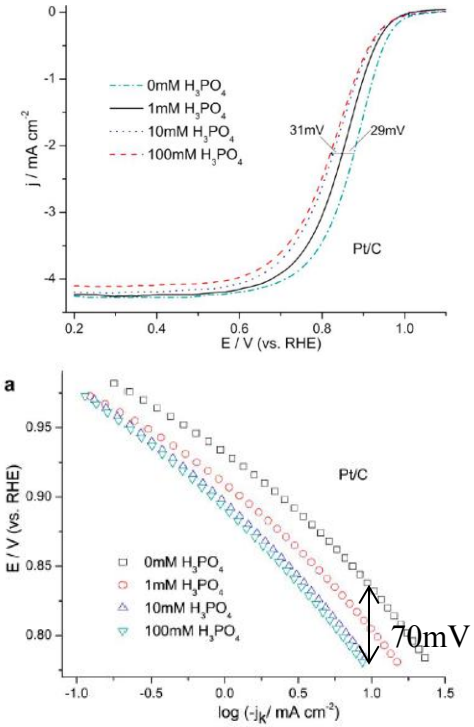


RDE Phosphate Poisoning

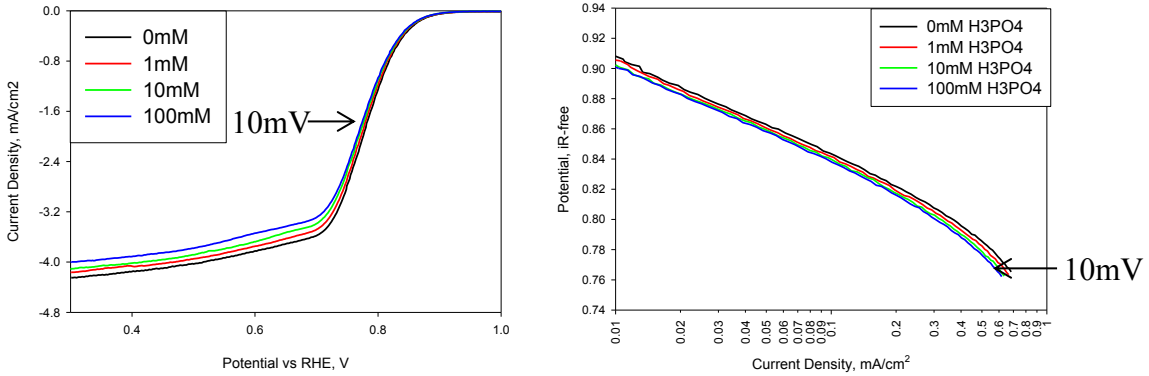
Pt (111)
Qinggang He et al, Physical Chemistry Chemical Physics 2010



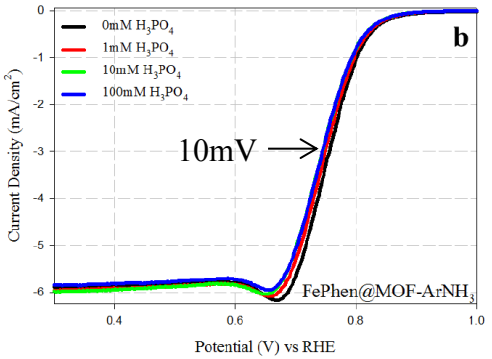
Pt/C
Qinggang He et al, Journal of Physical Chemistry C, 2013



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

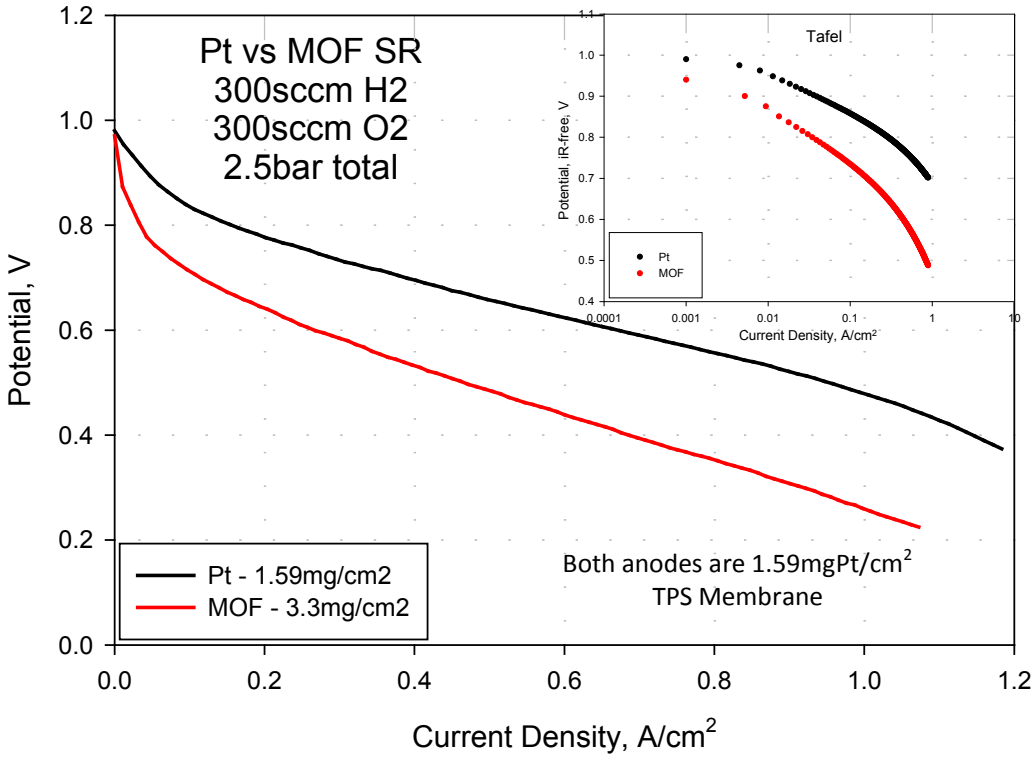


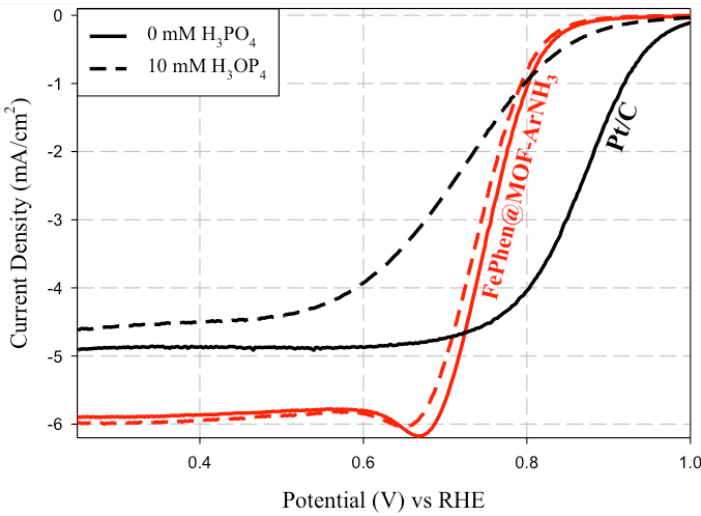
MOF Solution Reaction (MOF-SR)

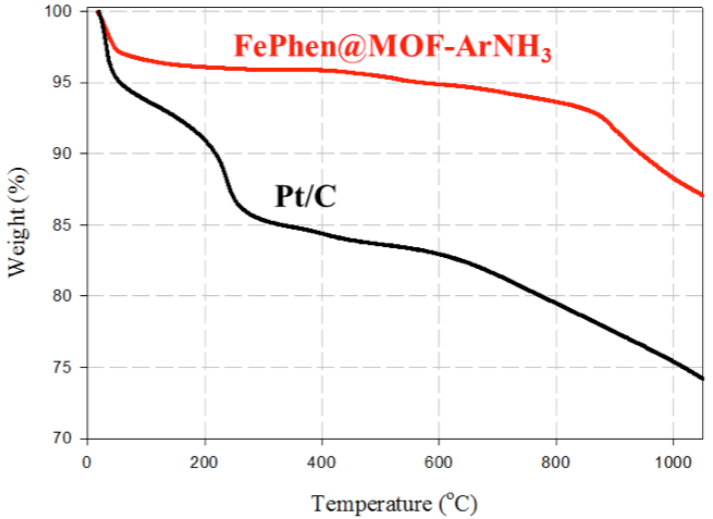


Measurements in a Phosphoric Acid Fuel Cell Interface-NEU

H_2/O_2 180˚C, TPS Membrane (Advent)

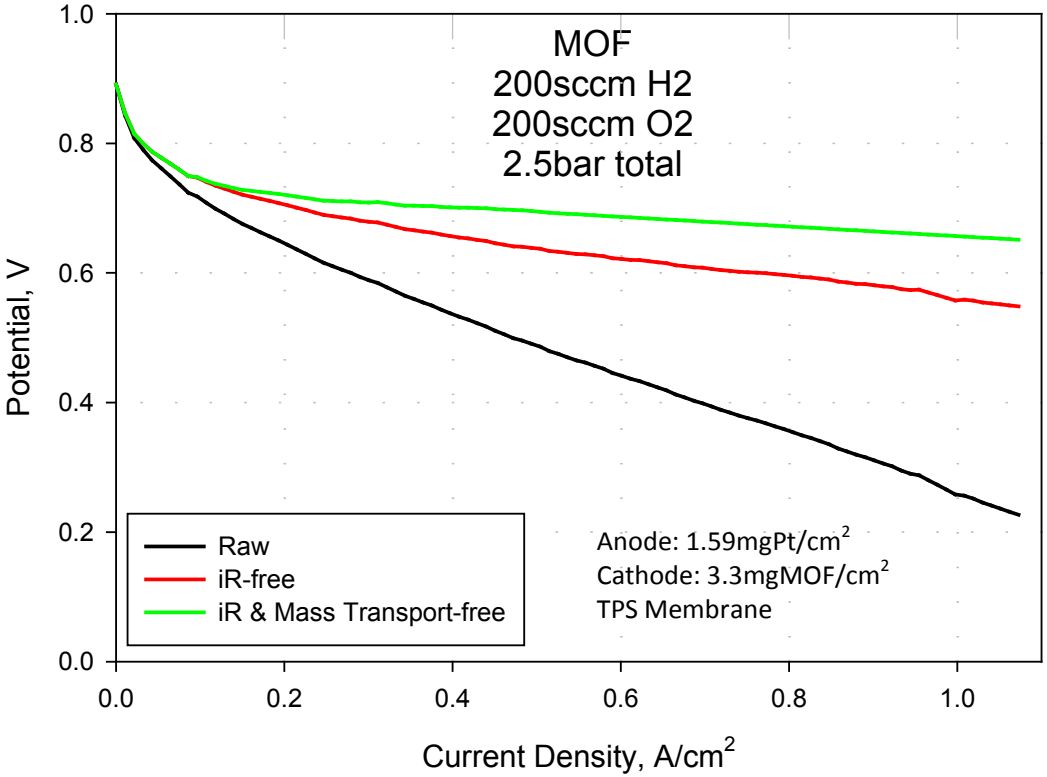






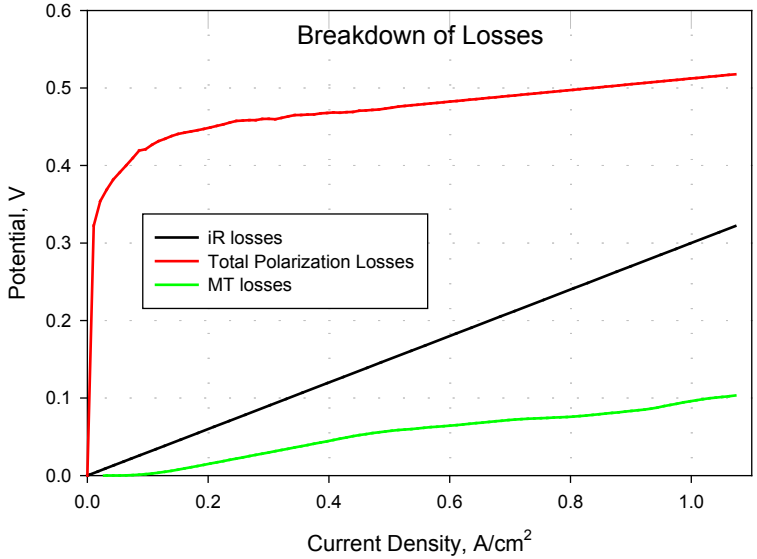
- Had to go to elevated backpressure (2.5bar total) to achieve DoE oxygen performance target due to flooding issues
- Flooding issues being addressed through new MEA preparation in conjunction with Advent Technologies

Analysis of performance losses in oxygen



New MEA formulation is being explored:

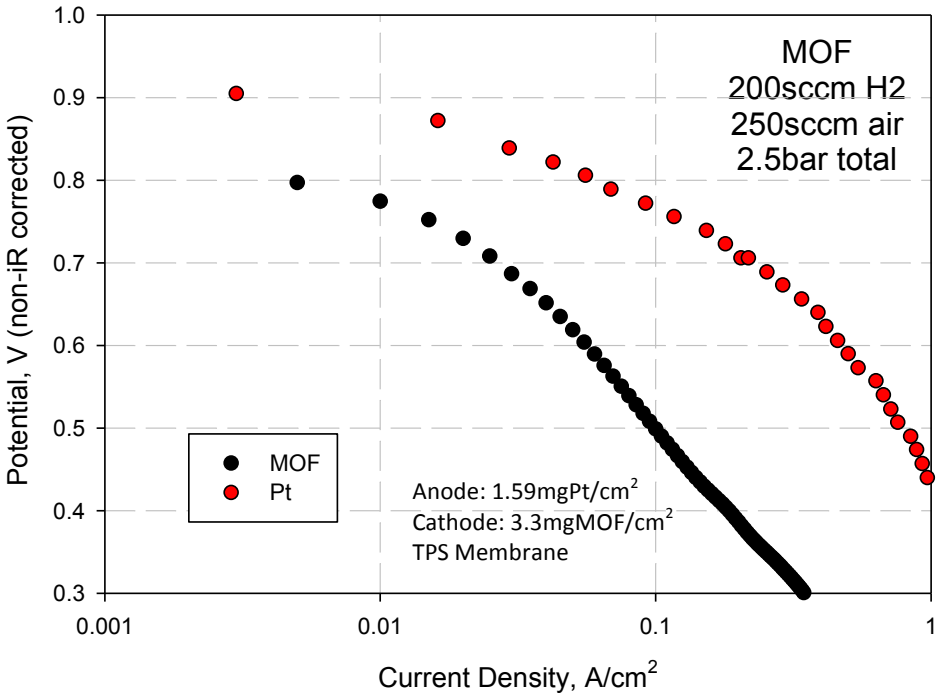
- Previous method did not include the presence of a binder within the cathode catalyst layer
  - Led to flooding of the catalyst layer, causing stability issues

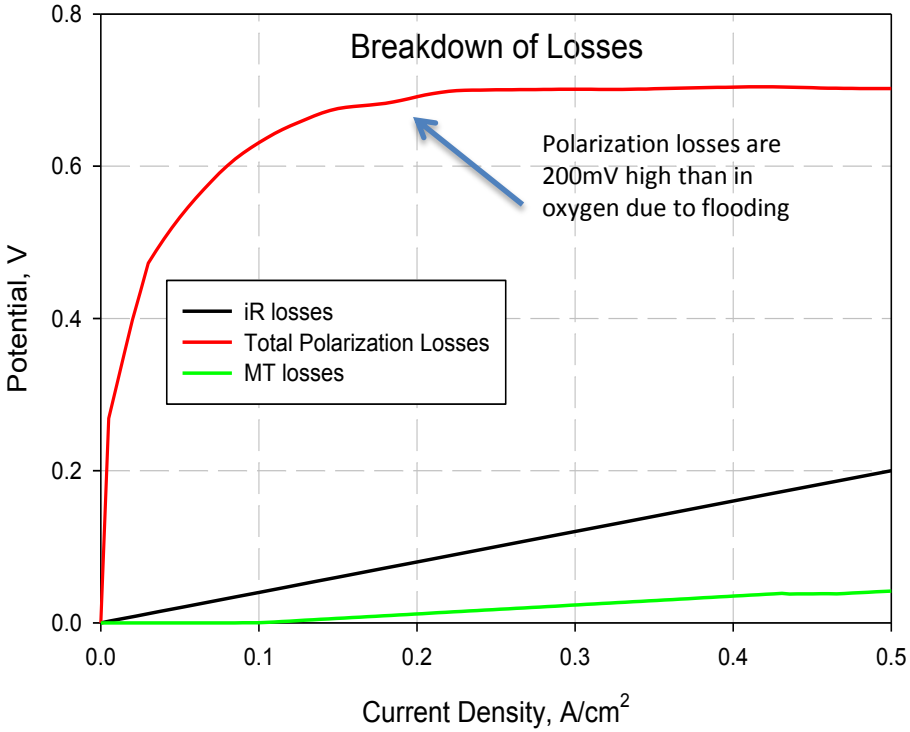


Preliminary air results

Previously-mentioned stability issues due to lack of binder were exacerbated in air (250mV O_2 gain @ 200mA/cm2)

- New data should be available in immediate future with new formulation
  - This should alleviate Polarization losses and make up necessary ground to DoE target





Summary Slide

- Task 1.1 Catalyst Preparation and Scale Up with MOF Chemistry: Inter and Intra batch variability and phosphate immunity demonstrated on MOF scale up catalysts for 5g batch size
  - Single cell testing in oxygen demonstrating 100mA/cm2 @ 0.7V & 2.5bar total pressure
    - Established target was at 1.5bar total pressure
      - Current changes in MEA preparation being implemented should allow for achievement of DoE target
- Task 2.1 Improving Mass Transport Characteristics
  - Single cell testing in air demonstrating 200mA/cm2 @ 0.6V & 2.5bar total pressure
    - Currently 100mV from achieving target
      - Again, changes currently being implemented should resolve discrepancy

Future Activities

- Major re-design of MEA fabrication techniques with input from Advent Technologies in order to transition from Pt to non-pgm
  - TPS & PBI membrane require very different methodologies for preparation
    - Teflon content
      - Optimizing content given much higher loading of non-pgm than Pt in typical MEA
    - Electrode and MEA annealing steps
      - Need much more fine-tuned control of temperature than previously had with muffle furnace
      - Multistep process in order to properly remove GDL/GDE additives
    - Adjustments made to hot-pressing techniques
      - Previous method was likely too much pressure, facilitated flooding from over-compression, which subsequently led to major issues with testing in air & performance degradation
        - » New technique will allow for specific % compression of MEA in order to prevent over-compression
  - These adjustments should cause significant improvement in stability and initial performance, allowing for achievement of DoE targets

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. Halevi (Industry, sub-contractor)
- Fuel Cell Energy, Inc., Danbury, CT: L. Lipp (Industry sub-contractor)
- Advent Technologies, Inc., Cambridge, MA: (Industry, special materials supplier): E. De Castro

Other collaborators:

Jean-Pol Dodelet: Canetique, Inc., Canada

Frederic Jaouen, 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.