HYDROGEN AND FUEL CELLS PROGRAM

2019 ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING

ARLINGTON, VA – APRIL 29 - MAY 1, 2019

Argonne NATIONAL LABORATORY

PEFC ELECTRODE STRUCTURES WITH ENCASED CATALYSTS TO ELIMINATE IONOMER ADSORPTION ON CATALYTIC SITES

DEBORAH MYERS AND AHMED FARGHALY

CHEMICAL SCIENCES AND ENGINEERING DIVISION

ARGONNE NATIONAL LABORATORY

Project ID# FC322

This presentation does not contain any proprietary, confidential, or otherwise restricted information

PROJECT OVERVIEW

Timeline

- Project Start Date: October 1, 2018
- Project End Date: September 30, 2020
- Percentage complete: 20%

Budget

- FY19 DOE Funding: $300K
- Total DOE Project Value: $750K
- Total DOE Funds Spent*: $108K

*as of 3/1/2019

Project Partners

- **Lead: Argonne National Laboratory**
  - Ahmed Farghaly, Debbie Myers, Rajesh Ahluwalia
  - Project management, catalyst synthesis, activity screening, MEA fabrication and initial testing, transport modeling
- **National Renewable Energy Laboratory**
  - K.C. Neyerlin
  - Operando studies of MEAs
- **Oak Ridge National Laboratory**
  - Karren More
  - Electron microscopy

Barriers

Barrier	2025 Target
A. Electrode Performance	**$\geq$300 mA/cm² at 800 mV** **$\geq$1000 mW/cm² at rated power (150 kPa, 94 °C, >0.67 V)**
B. Cost	**$8 kW/$g_{pgm}$, <$40 kW_e system (<$20 kWe net stack),** **$\leq$0.125 mg_{PGM}/cm²**
C. Durability	**<40% loss of initial catalytic mass activity at 900 mV on O_2; <30 mV loss at 0.8 A/cm² on air; <30 mV loss at 1.5 A/cm² on air**

RELEVANCE, OBJECTIVE, AND IMPACT

- Project Objective
  - This project intends to address the lack of sufficient areal power density at rated power for an automotive PEFC stack and the lack of sufficient performance durability due to direct contact between the proton-conducting and electron-conducting components of the PEFC cathode catalyst layer with the platinum catalyst surface.
  - Protect Pt and Pt_xCo_{1-x} nanoparticle cathode catalysts from direct contact with the proton-conducting and electron-conducting phases while also maintaining sufficient oxygen, proton, and electron transport to the catalytic sites.

- Impact on DOE Targets
  - If successful, this project will improve the high current density hydrogen-air performance of PEFCs having Pt loadings of 0.125 mg-Pt/cm^2 versus the state-of-the-art PEFCs which use carbon-supported Pt of PtCo catalysts, while also maintaining the performance over the 8,000 h operating time target.
  - Ultimate Project Goals:
    - Exceed 8 kW/g_{PGM}, >1.0 W/cm^2 (150 kPa, 94 ℃, >0.67 V)
    - <40% loss in cathode catalyst mass activity, <30 mV loss at 0.8 A/cm^2, and <30 mV loss at 1.5 A/cm^2 (cell subjected to the catalyst and support accelerated stress tests, respectively)

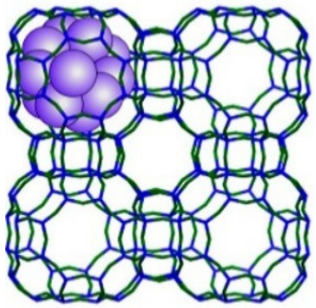
ISSUES ADDRESSED AND APPROACH

- Problem Statement and Issues Addressed:
  - The performance of PEFC cathodes is insufficient to reach stack power density targets at high current densities (>1 A/cm²) when using low loadings of Pt, ≤0.1 mg-Pt/cm², needed to achieve stack cost targets
  - A major portion of high current density losses is related to interaction between the catalyst surface and the perfluorosulfonic acid ionomer inhibiting ORR kinetics and oxygen transport to the catalytic sites
  - Pt and Pt alloy catalysts supported on high surface area carbon lose electrochemically-active surface area through particle migration and coalescence and dissolution and re-precipitation
  - Alloying metals are lost from Pt alloy cathode catalysts during load cycling, causing loss of ORR activity
  - Carbon supports corrode at the catalyst/support interface causing loss of electrical contact with the particles and loss of catalyst electrochemically-active surface area

- Approach to Addressing Issues: Encase Pt and Pt alloy catalyst particles in the cages and pores of zeolites
  - Eliminates direct contact of catalyst particles with ionomer and with carbon
  - Eliminates particle migration
  - May decrease acidity of the environment around catalyst particles

APPROACH: INTRODUCTION TO CONCEPT

- Zeolites are alumino-silicates forming ordered structures with well-defined channels and cavities
- Zeolites are known to “size sort” molecules due to the well-defined channels (e.g., 5.5 Å diameter in ZSM-5) that allow passage of molecules with diameters smaller than the channel diameter, but exclude larger species from the interior of the zeolite
- Zeolites are used in the gas-phase catalysis industry to prevent sintering and loss of catalyst surface area under high-temperature reaction conditions
- Molecular diameter of oxygen is 3.46 Å, ionomer forms rods of 2-2.5 nm diameter in solution, allowing exclusion of PFSA, but access of oxygen into zeolite cages
- Zeolites are proton conductors; conductivities as high as 0.1 S/cm demonstrated
- Zeolites are poor electron conductors; carbon will be necessary in electrode layer to conduct electrons



Metal nanoparticle
in ZSM-5 zeolite

Image source: http://www.cchem.berkeley.edu/molsim/teaching/fall2009/mto/cat.html

APPROACH: MILESTONES AND GO/NO-GO

QTR	Due Date	Progress Measures, Milestones, Deliverables	Status
Q1	12/31/2018	Synthesize more than forty Pt and Pt_xCo_{1-x}@Zeolite materials and succeed in incorporating at least 10 wt% metal in the interior of the Zeolite cages for at least ten of these materials.	Complete: 62 unique Pt catalysts synthesized
Q2	3/31/2019	Determine the ORR activity and activity stability of the down-selected Pt and Pt_xCo_{1-x}@Zeolite catalysts in RDE and MEA, with activity goals of 0.2 A/mg_{Pt} for Pt@Zeolite catalyst and 0.75 A/mg_{Pt} for Pt_xCo_{1-x}@Zeolite at 0.9 $V_{HFR\text{-}free}$.	In progress, Pt@Zeolite activity in RDE of >0.2 A/mg_{Pt} achieved
Q3	6/30/2019	Determine local oxygen transport resistance from oxygen limiting current measurements for unoptimized CCL structures based on Pt@Zeolite and Pt_xCo_{1-x}@Zeolite, with a goal of $\leq$10 S/cm while also maintaining ORR activities achieved in Q2.	
Q4	9/30/2019	Achieve ORR activities of 0.4 A/mg-Pt for Pt@Zeolite catalyst and 1.5 A/mg_{Pt} for Pt_xCo_{1-x}@Zeolite at 0.9 $V_{HFR\text{-}free}$ in RDE testing and 0.22 A/mg_{Pt} for Pt@Zeolite catalyst and 0.81 A/mg_{Pt} for Pt_xCo_{1-x}@Zeolite at 0.9 $V_{HFR\text{-}free}$ in MEA testing. Achieve <40% loss in catalyst mass activity and <30 mV loss at 0.8 A/cm^2 in an MEA after catalyst and support AST cycling (30,000 and 5,000 cycles, respectively).	Go/No-Go
Q5	12/31/2019	Achieve ORR activities of 0.3 A/mg_{Pt} for Pt@Zeolite catalyst and 1.0 A/mg_{Pt} for Pt_xCo_{1-x}@Zeolite at 0.9 $V_{HFR\text{-}free}$ in MEA testing. Achieve <40% loss in catalyst mass activity and <30 mV loss at 0.8 A/cm^2 in an MEA after catalyst and support AST cycling (30,000 and 5,000 cycles, respectively).	
Q6	3/31/2020	Demonstrate local oxygen transport resistance of <10 S/cm for Pt and Pt_xCo_{1-x}@Zeolite CCLs and catalyst utilization (dry proton accessibility) of >60% down to 30% RH.	
Q7	6/30/2020	Fabricate and test the MEA performance of CCLs based on two down-selected Pt and Pt_xCo_{1-x}@Zeolite catalysts, with a performance of >0.7 W/cm^2 (H_2-Air, 150 kPa, 94°C, >0.67 V) and durability goal of <30 mV loss at 0.8 A/cm^2, and <30 mV loss at 1.5 A/cm^2 after 30,000 or 5,000 catalyst or support AST cycles.	
Q8	9/30/2020	MEA construction/composition, based on Pt@Zeolite or Pt_xCo_{1-x}@Zeolite-containing CCLs, that exceeds 8 kW/g_{PGM}, >1.0 W/cm^2 (150 kPa, 94°C, >0.67 V) and has <40% loss in cathode catalyst mass activity, <30 mV loss at 0.8 A/cm^2, and <30 mV loss at 1.5 A/cm^2 when subjected to the catalyst and support accelerated stress tests (ASTs), respectively.	

COLLABORATION, COORDINATION, SCHEDULE

Task No.	Description	Organization	BP1 Activity Level	BP2 Activity Level
Task 1	Synthesis and characterization of Pt@Zeolite, Pt_xCo_{1-x}@Zeolite powders	ANL	1	0.75
Task 2	Catalyst-ionomer ink synthesis and optimization	ANL, NREL	0.25	0.5
Task 3	Screening of ORR activity and electronic conductivity using aqueous hydrodynamic techniques	ANL	0.25	0.25
Task 4	Fabrication and performance testing of Pt@Zeolite and Pt_xCo_{1-x}@Zeolite membrane-electrode assemblies	ANL, NREL	0.7	1.25
Task 5	Characterization of catalyst powders and cathode catalyst layers	ORNL	0.5	0.5
Task 6	Operando differential cell measurements of electrochemical kinetics and transport	NREL	0.3	0.75
Task 7	Modeling kinetic and transport processes	ANL	0	0.5

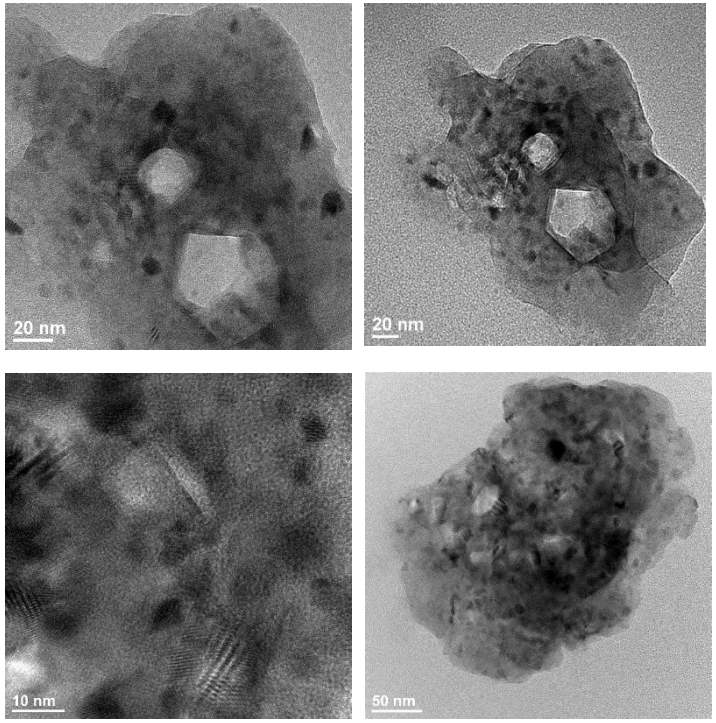
ACCOMPLISHMENTS

- Sixty-two Pt-based catalysts were synthesized by incipient wetness/ion-exchange using a cationic Pt complex and two zeolite types (ZSM-5 and mordenite)
- Three Pt loadings were targeted: 1, 5, and 10 wt%. Actual loadings were determined by inductively-coupled plasma optical emission and X-ray fluorescence spectroscopies.
- Ion-exchange was followed either by solution phase reduction and/or heat treatment in a reducing gas to form metallic Pt from cationic complex
- Formation of conductive carbon, external to the zeolite cages, was explored by adding polyvinylpyrrolidone or pyrrole to the Pt@Zeolite prior to heat treatment
- *In situ* formation of a protective, but porous silicate layer was also explored by incorporating tetraethyl orthosilicate 3-(aminopropyl)trimethoxysilane during synthesis
- Post-deposition/reduction annealing to enhance Pt crystallinity was explored, using three annealing temperatures
- Addition of Ketjen, Black Pearls, or chemically-oxidized Black Pearls to the catalyst ink was necessary to form uniform, electrically-conductive layers for ORR activity screening using RDE.

TEM CHARACTERIZATION OF PT@ZSM-5

- TEM images show two locations for Pt with respect to ZSM-5
  - Pt particles dispersed across surface of zeolites
  - Pt particles inside zeolite cages
- Zeolites are crystalline, but agglomerated into irregular shapes
- In the samples incorporating polypyrrole in the synthesis, the Pt particles are covered by an amorphous carbon shell

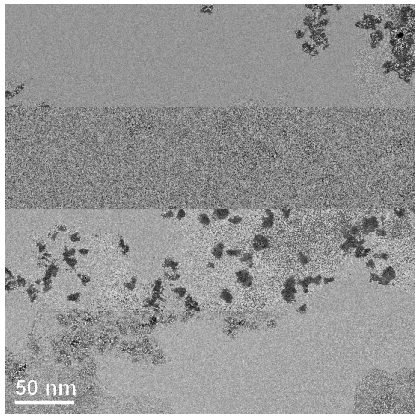
10 wt% Pt@ZSM-5-Polypyrrole Room Temperature

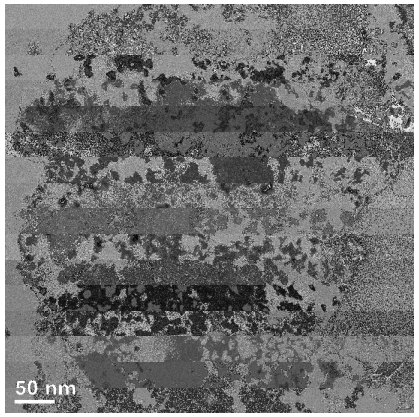


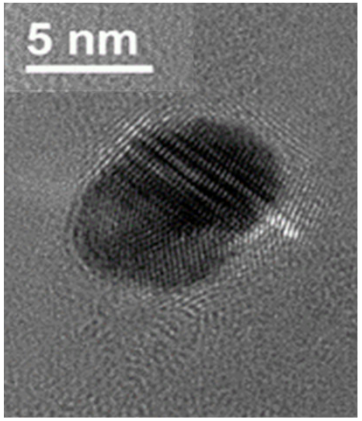
Argonne NATIONAL LABORATORY

TEM CHARACTERIZATION OF PT@ZSM-5

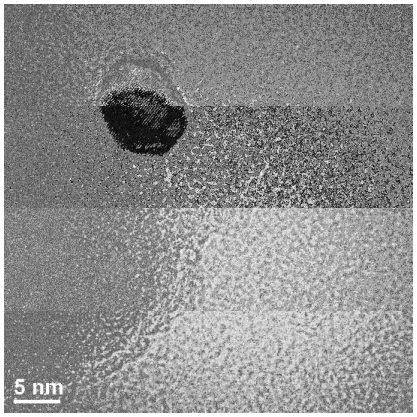
10 wt% Pt@ZSM-5-Polypyrrole
Room Temperature

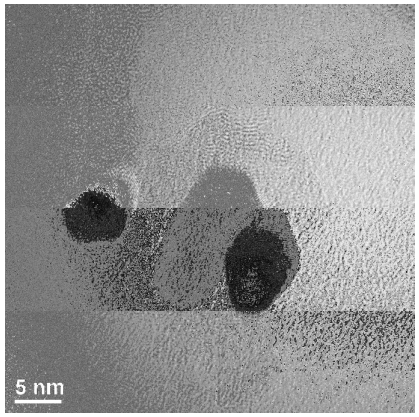


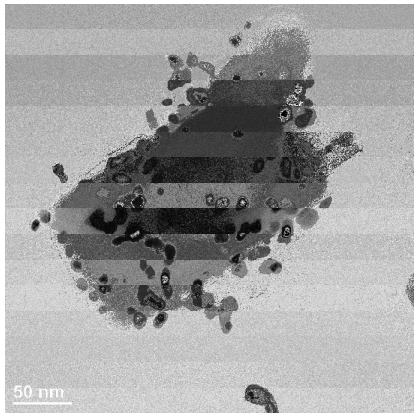




10 wt% Pt-ZSM-5-Polypyrrole
600°C

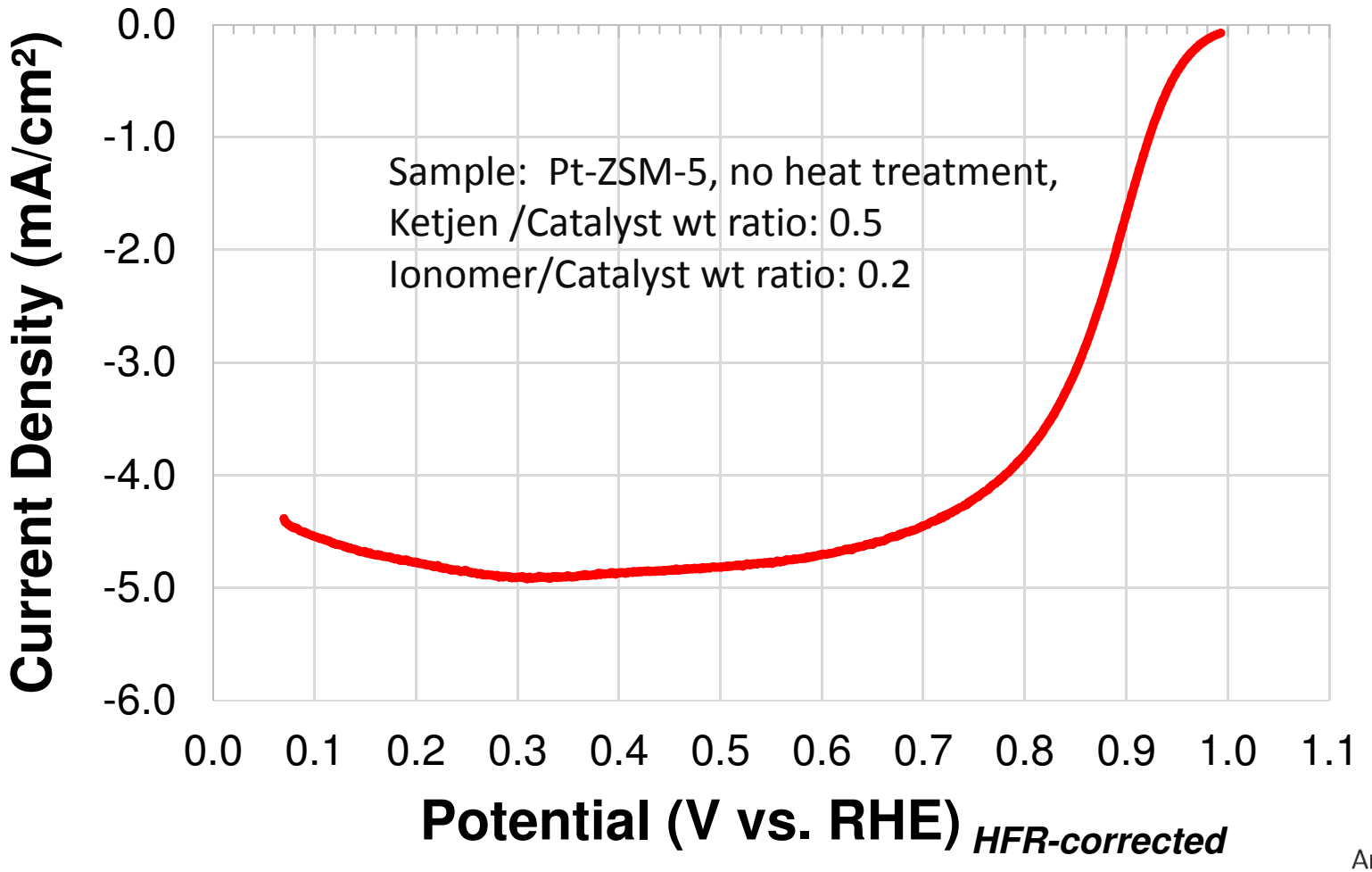






ACCOMPLISHMENT: OXYGEN REDUCTION REACTION ACTIVITY SCREENING OF PT@ZSM-5

Thin-film rotating disk electrode technique. Oxygen-saturated, room temperature 0.1 M $HClO_4$ electrolyte. Rotation rate: 1600 rpm; Pt loading on glassy carbon tip: 9 µg/cm²; Scan rate 10 mV/s; Anodic-going scan.



ACCOMPLISHMENT: OXYGEN REDUCTION REACTION MASS ACTIVITIES EVALUATED

Summary of Oxygen Reduction Reaction Mass Activities
Thin Film Rotating Disk Electrode Technique

Catalyst, additive, heat-treatment temp., carbon content	Mass activity at 0.9 $V_{HFR\ free}$ (mA/mg_{Pt})
Pt-ZSM-5, no heat treatment, 33 wt% Ketjen	284
Pt-ZSM-5, 600℃, 50 wt% Ketjen	41.6
Pt-ZSM-5, 600℃, 33 wt%	42.1
Pt-ZSM-5, Pyrrole, 600℃, 33 wt% Ketjen	113
Pt-ZSM-5, 1050℃, 33 wt% Ketjen	6.1
Pt-ZSM-5, PVP, 1050℃, 33 wt% Ketjen	2.6
Pt-ZSM-5, Pyrrole, 1050℃, 33 wt% BP	4.3
Pt-ZSM-5,TEOS, 1050℃, 33 wt% BP	2.1
Pt-ZSM-5, 600℃, 33 wt% Oxidized BP	23.7
Pt-ZSM-5, 600℃, 33 wt% Ox. BP, Polypyrrole binder, no PFSA	30.5

PVP=polyvinylpyrrolidone; TEOS=tetraethyl orthosilicate; BP=Black Pearls; PFSA=Perfluorosulfonic acid

Highlight: target of >0.2 A/mg_{Pt} at 0.9 V achieved

Argonne NATIONAL LABORATORY

REMAINING CHALLENGES AND FUTURE WORK

- Eliminate Pt deposition on the outside of zeolite cages and/or deposit a protective, but porous shell over the external Pt particles
- Incorporate higher loadings of Pt and Pt_xCo_{1-x} into/on zeolites (>10 wt%)
- Demonstrate that zeolite is protecting Pt and Pt_xCo_{1-x} particles from poisoning by ionomer by determining ORR activity with and without ionomer in thin film
- Demonstrate that preventing direct contact of catalyst particles with amorphous carbon that carbon corrosion-related degradation of catalyst electrochemically-active surface area is eliminated
- Fabricate and evaluate performance and durability of membrane-electrode assemblies using down-selected Pt@Zeolite and Pt_xCo_{1-x}@Zeolite cathode catalysts

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

SUMMARY

- Sixty-two Pt-based catalysts were synthesized
  - Two types of zeolites, three metal loadings, two Pt precursor reduction methods, presence or absence of stabilizing agent, and three post-reduction heat treatments
- TEM characterization showed that Pt particles were deposited both inside the zeolite cavities and on the surface of the zeolites
- Methods are being developed to eliminate or decrease metal particle formation on exterior of zeolite and/or to protect these particles
- The oxygen reduction reaction activity of ten of these sixty-two catalysts was screened using the thin-film RDE technique
  - Highest activity of 284 mA/mg_{Pt} achieved with 10 wt% Pt@ZSM-5 with no post-deposition annealing
- Immediate next steps:
  - Evaluation of ORR, with and without ionomer, of select remaining Pt@ZSM-5 and Pt@Mordenite samples
  - Synthesis of Pt_xCo_{1-x}@ZSM-5 with varying x and Pt_xCo_{1-x} loading in ZSM-5
  - MEA fabrication and evaluation of most active Pt@Zeolite and Pt_xCo_{1-x}@Zeolite catalysts

RESPONSE TO PREVIOUS YEAR'S REVIEWERS' COMMENTS

- This is the first year this project is being reviewed