HYDROGEN AND FUEL CELLS PROGRAM 2020 ANNUAL PROGRESS REPORT



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



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Project ID# FC322

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# **PROJECT OVERVIEW**

### Timeline

- Project Start Date: October 1, 2018
- Project End Date: September 30, 2020
- Percentage complete: 65%

### Budget

- FY20 DOE Funding: \$450K
- Total DOE Project Value: \$750K
- Total DOE Funds to ANL: \$450K
- Total DOE Funds Spent: \$456K\*
  \*as of 4/26/2020

### **Project Partners**

- Lead: Argonne National Laboratory
  - Ahmed A. Farghaly, Debbie J. 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

- David Cullen and Michael Zachman
- Electron microscopy, electron energy loss spectroscopy

#### **Barriers**

Barrier	2025 Target
A. Electrode Performance	≥300 mA/cm² at 800 mV ≥1000 mW/cm² at rated power (150 kPa, 94°C, >0.67 V)
B. Cost	\$8 kW/g <sub>pgm</sub> , <\$40 kW <sub>e</sub> system (<\$20 kWe net stack), <u>&lt;</u> 0.125 mg <sub>PGM</sub> /cm²
C. Durability	<40% loss of initial catalytic mass activity at 900 mV on $O_2$ ; <30 mV loss at 0.8 A/cm <sup>2</sup> on air; <30 mV loss at 1.5 A/cm <sup>2</sup> 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<sub>x</sub>Co<sub>1-x</sub> 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<sup>2</sup> versus the state-of-theart 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<sub>PGM</sub>, >1.0 W/cm<sup>2</sup> (150 kPa, 94°C, >0.67 V)
  - <40% loss in cathode catalyst mass activity, <30 mV loss at 0.8 A/cm<sup>2</sup>, and <30 mV loss at 1.5 A/cm<sup>2</sup> (cell subjected to the catalyst and support accelerated stress tests, respectively)



## **ISSUES ADDRESSED**

### Problem Statements and Issues Addressed:

 The performance of PEFC cathodes is insufficient to reach stack power density targets at high current densities

(>1 A/cm<sup>2</sup>) when using low loadings of Pt,  $\leq$ 0.1 mg-Pt/cm<sup>2</sup>, 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 (PFSA) ionomer inhibiting oxygen reduction reaction (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 electrode fabrication and 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





Ni to Pt ratio in a PtNi alloy/Ketjen catalyst before and after incorporation into a catalyst-coated membrane





# **ISSUES WITH CARBON-SUPPORTED CATALYST PARTICLES**



- Graphitized carbon (EA) is more stable when cycling up to high potentials than either HSC (E-Type) or Vulcan (V-type)
- Extents of corrosion linked to formation of carbon oxides and interaction of these oxides with Pt hydroxide and oxide and water



 Catalyst particles migrate along surface of more stable carbons and lose surface area by coalescence



# **APPROACH: INTRODUCTION TO CONCEPT**

- 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
- 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
  - 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

Pt or Pt alloy nanoparticle



3D Porous Inorganic frameworks with pore size < 2 nm



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 <sub>Pt</sub> for Pt@Zeolite catalyst and 0.75 A/mg <sub>Pt</sub> for Pt_xCo_{1-x}@Zeolite at 0.9 V <sub>HFR-free</sub> .	Pt@Zeolite activity in RDE of >0.2 A/mg <sub>Pt</sub> 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 <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 <sub>Pt</sub> for $Pt_xCo_{1-x}@Zeolite$ at 0.9 $V_{HFR-free}$ in RDE testing and 0.22 A/mg <sub>Pt</sub> for Pt@Zeolite catalyst and 0.81 A/mg <sub>Pt</sub> for Pt_xCo_{1-x}@Zeolite at 0.9 $V_{HFR-free}$ in MEA testing. Achieve <40% loss in catalyst mass activity and <30 mV loss at 0.8 A/cm <sup>2</sup> 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 <sub>Pt</sub> for Pt@Zeolite catalyst and 1.0 A/mg <sub>Pt</sub> for $Pt_xCo_{1-x}$ @Zeolite at 0.9 V <sub>HFR-free</sub> in MEA testing. Achieve <40% loss in catalyst mass activity and <30 mV loss at 0.8 A/cm <sup>2</sup> 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 <sup>2</sup> (H <sub>2</sub> -Air, 150 kPa, 94°C, >0.67 V) and durability goal of <30 mV loss at 0.8 A/cm <sup>2</sup> , and <30 mV loss at 1.5 A/cm <sup>2</sup> after 30,000 or 5,000 catalyst or support AST cycles.	*
Q8	9/30/2020	MEA construction/composition, based on Pt@Zeolite or Pt <sub>x</sub> Co <sub>1-x</sub> @Zeolite-containing CCLs, that exceeds 8 kW/g <sub>PGM</sub> , >1.0 W/cm <sup>2</sup> (150 kPa, 94°C, >0.67 V) and has <40% loss in cathode catalyst mass activity, <30 mV loss at 0.8 A/cm <sup>2</sup> , and <30 mV loss at 1.5 A/cm <sup>2</sup> when subjected to the catalyst and support accelerated stress tests (ASTs), respectively.	*

\*Issues with non-uniformity of commercially-available zeolites and electrical conductivity necessitated rescoping of project to focus on zeolite synthesis and carbon incorporation/deposition



# SUMMARY OF SYNTHESIS ACCOMPLISHMENTS

- Sixty-two Pt-based catalysts were synthesized by incipient wetness/ion-exchange using a cationic Pt complex and two commercial zeolites (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 catalystionomer ink was necessary to form uniform, electrically-conductive layers for ORR activity screening using RDE



# SUMMARY OF SYNTHESIS ACCOMPLISHMENTS

- Electron-conducting zeolite nanocrystals (ZNC) were synthesized by chemical vapor deposition (CVD) of graphene-like carbon
- Electron-conducting hollow zeolite nanocrystals (HZNC) were synthesized by CVD of graphene-like carbon
- Gram synthesis of first electron-conducting encased catalyst Pt@HZNC via two novel synthesis routes. Synthetic method development necessary due to the observed ability of Pt to oxidize the CVD graphene precursors to carbon monoxide and carbon dioxide
  - Sol-gel-assisted CVD of graphene-like carbon to encase Pt and Pt alloy nanoparticles within a hollow 3D inorganic zeolitic framework
  - Hydrothermal synthesis of encased Pt and Pt alloy nanoparticles between the graphene layers within a hollow electron-conductive 3D inorganic zeolitic framework



# PT@COMMERCIAL 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 600°C







Sixty-two unique materials were synthesized from commercial zeolites, varying Pt loading, incorporating PtCo, incorporating carbon using polypyrrole, varying heat treatment temperature, etc. Pt loading in interior of zeolites was minimal (1-2 wt%)

# OXYGEN REDUCTION REACTION ACTIVITY SCREENING OF PT@ZSM-5

Thin-film rotating disk electrode technique. Oxygen-saturated, room temperature 0.1 M HClO<sub>4</sub> electrolyte. Rotation rate: 1600 rpm; Pt loading on glassy carbon tip:  $9 \mu g/cm^2$ ; Catalyst/**Ketjen** wt ratio **0.5**, Ionomer/Catalyst wt ratio 0.2; Scan rate 10 mV/s; Anodic-going scan



# SUMMARY OF OXYGEN REDUCTION REACTION MASS ACTIVITIES OF PT @ COMMERCIAL ZSM-5

#### 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 <sub>HFR-free</sub> (mA/mg <sub>Pt</sub> )	
Pt-ZSM-5, no heat treatment, 33 wt% Ketjen	284	
Pt-ZSM-5, 600°C, 50 wt% Ketjen	41.6	
Pt-ZSM-5, 600°C, 33 wt%	42.1	
Pt-ZSM-5, Pyrrole, 600°C, 33 wt% Ketjen	113	
Pt-ZSM-5, 1050°C, 33 wt% Ketjen	6.1	
Pt-ZSM-5, PVP, 1050°C, 33 wt% Ketjen	2.6	
Pt-ZSM-5, Pyrrole, 1050°C, 33 wt% BP	4.3	
Pt-ZSM-5,TEOS, 1050°C, 33 wt% BP	2.1	
Pt-ZSM-5, 600°C, 33 wt% Oxidized BP	23.7	
Pt-ZSM-5, 600°C, 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<sub>Pt</sub> at 0.9 V achieved



# SYNTHESIS OF HOLLOW NANO-ZEOLITES TO INCREASE PT LOADING

2019 AMR reviewer's comment "...getting Pt or PtCo in zeolite cages will be very challenging"

Pt particles in hollow Nano-zeolite crystals nano-zeolite crystals 1.00um 50 mm x35.0k (b) (d) ~5-10 nm diameter Pt particles x400k 100nm 20 nm

# SOL-GEL ASSISTED SYNTHESIS OF ZEOLITE NANO-CRYSTALS

Goal: Address issues of inhomogeneity and low internal Pt loadings obtained with commercial zeolites



- Synthetic procedure for forming uniform nano-ZSM-5 cuboids developed
- The presence of Pt and Co ions during nano-zeolite crystal growth affected their size and morphology



## SOL-GEL ASSISTED CARBON DEPOSITION TO ENCASE PT AND PT ALLOY NANOPARTICLES WITHIN AN ELECTRON-CONDUCTING HOLLOW 3D INORGANIC ZEOLITIC FRAMEWORK

Synthetic steps for forming encased Pt nanoparticles:

- Synthesis of nano-zeolites
- Synthesis of nano-zeolites with Pt<sub>x</sub>O<sub>y</sub>H<sub>z</sub>
- Synthesis of Pt<sub>x</sub>O<sub>y</sub>H<sub>z</sub> encased in hollow zeolites nanocrystals (Pt<sub>x</sub>O<sub>y</sub>H<sub>z</sub> @HZNC)
- Reduction of Pt<sub>x</sub>O<sub>y</sub>H<sub>z</sub> with hydrogen or sodium borohydride to form Pt particles encased in hollow nano-zeolites (Pt@HZNC)
- Addition of graphene-deposition-aid (GrDA) on surface of hollow nano-zeolites (Pt@HZNC@GrDA)
- Graphene deposition on outside surface of hollow nanozeolites (Pt@HZNC@GrDA@Gr)











### SOL-GEL ASSISTED SYNTHESIS OF GRAM-SCALE PT NANOPARTICLES ENCASED WITHIN AN ELECTRON-CONDUCTIVE HOLLOW 3D INORGANIC ZEOLITIC FRAMEWORK

Goal: Address issue of zeolites poor electrical conductivity



### HYDROTHERMAL SYNTHESIS OF PT NANOPARTICLES ENCASED IN GRAPHENE LAYERS WITHIN A HOLLOW ELECTRON-CONDUCTING 3D INORGANIC ZEOLITIC FRAMEWORK

Goal: Address issue of poor electrical conductivity of zeolites





# NATURE OF THE DEPOSITED CARBON IN THE ENCASED PT NANOPARTICLE CATALYST



Intensity of  $\pi^*$  and  $\sigma^*$  bands indicative of level of graphitization

Reference: L.A.J. Garvie *et al.,* Am. Mineral 79 (1994) 411.

Carbon EELS fine structure resembles that of graphitic carbon in the catalysts



 Thermal stability via thermogravimetric analysis indicates that catalysts do not contain amorphous carbon and the deposited carbon is graphene-like

## **ELECTRONIC CONDUCTIVITY OF NANO-ZEOLITES ACHIEVED**



Voltammetry of as-prepared conductive ZSM-5 nanocrystals at different potential scan rates: 10, 50, 100, 200, 300, 400 and 500 mV s<sup>-1</sup>; Electrolyte: room temp. Ar-sat. 0.1 M HClO<sub>4</sub>



Background- and iR-corrected ORR voltammograms. RDE loading: 18  $\mu$ g<sub>Pt</sub>cm<sup>-2</sup>; Electrolyte: room temp. O<sub>2</sub>-sat. 0.1 M HClO<sub>4</sub>; Rotation rate: 1600 rpm; Scan rate: 10 mV s<sup>-1</sup>; anodic-going scan

- Background voltammetry lacks a resistive slope attesting to efficacy of carbon deposition in imparting electron conductivity to ZSM-5 nano-zeolites
- Encased Pt particles are sinter resistant during heat treatment while non-encased Pt particles underwent sintering and lost ORR activity
- Encased Pt may not be completely accessible
- The deposited carbon is more effective than addition of carbon black to catalystionomer ink in providing electron transport to Pt nanoparticles.



## **DURABILITY OF GR@PT: SUPPORT AST IN RDE**





# **REMAINING CHALLENGES AND FUTURE WORK**

- Develop method to remove zeolite without collapsing hollow carbon structure
  - ✓ Utilize two-step, slower dissolution procedure
  - Break up nano-zeolite agglomerates before adding GrDA layer
- Overcome the mass transport issue
  - Engineering nanopores/nanocracks < 2 nm via KOH treatment</p>
  - Increase the hydrophilicity of the mother zeolite and thus the final catalyst to improve ionomer interaction with zeolite surface
- Increase uniformity of Pt loading inside nano-zeolites
- Demonstrate that zeolite is protecting Pt and Pt<sub>x</sub>Co<sub>1-x</sub> particles from poisoning by ionomer by determining ORR activity via RDE with and without ionomer in thin film
- Repeat support and catalyst AST RDE evaluation of Gr@Pt
  - Compare to commercial catalyst with similar Pt particle size distribution and with various carbon supports
- Fabricate and evaluate performance and durability of membrane-electrode assemblies using down-selected carbon-encased Pt and carbon-encased Pt<sub>x</sub>Co<sub>1-x</sub> cathode catalysts



# SUMMARY

- Sixty-two Pt-based catalysts were synthesized from commercial zeolites
  - Two types of commercial 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
- The oxygen reduction reaction activity of these sixty-two catalysts was screened using the thin-film RDE technique
  - ✓ Highest activity of 284 mA/mg<sub>Pt</sub> achieved with 10 wt% Pt@ZSM-5 with no postdeposition annealing
- To address poor selectivity of particles for interior of zeolite, developed a synthetic procedure for forming nano-zeolites around Pt and Co precursors
- To address poor electronic conductivity of zeolites, developed a method for depositing carbon on zeolites
- To address low loading of metal particles in zeolite, developed a method for forming "hollow" zeolites, depositing Pt in zeolite, removing zeolite, thus encasing Pt in carbon

### **RESPONSE TO REVIEWERS' COMMENTS FROM 2019 ANNUAL MERIT REVIEW**

- "This is an excellent, but very challenging, approach. If successful, it will boost the performance (areal power density) and durability too, as Pt nanoparticles are not in contact with the ionomer directly."
- "There are many questions or uncertainties that would have to work out for this approach to work."
- "Carbon inclusion is laid out, but the seemingly random inclusion could still lead to significant metal deactivation. This seems to be a key risk in the project."
- "First, the zeolites have insufficient conductivity, and placing the catalyst within an insulating cage is a dubious start. The encaged catalyst's having electrical and ionic connectivity through the catalyst layer will be very difficult to achieve."
  - Response: For all the commercial zeolites, we did indeed need to add carbon to the electrode layer for sufficient conductivity. To address this issue and the issue of Pt depositing both on the inside and outside of the zeolite cage, we successfully prepared highly conductive zeolite nanocrystals and hollow nanocrystals via growing a graphene-like carbon coating.



### **RESPONSE TO REVIEWERS' COMMENTS FROM 2019 ANNUAL MERIT REVIEW**

- "The key concerns would be processing cost and quality control."
  - Response: Unlike most of the synthesis protocols for nanomaterials which are suffering from the poor reproducibility. The developed protocol for the sol-gel synthesis of the encased Pt/Pt alloy nanoparticle catalysts is reproducible and scalable. We started by preparing milligram amounts and now we can produce gram-level amounts (e.g., 10 grams).
- "Cost assessment analysis is required to address how the encased Pt/Pt alloy nanoparticle catalysts are standing from the economic point of view."
  - *Response:* The developed synthesis protocol is straightforward, reproducible, and scalable. However, a cost assessment analysis is required to determine the mass production economics of the encased Pt/Pt alloy nanoparticle catalyst synthesis procedure.
- The most challenging thing will be to avoid Pt deposition outside or on the zeolite cage."
  - *Response:* We successfully encased the catalyst (e.g., Pt) nanoparticles inside a hollow zeolite nanobox and TEM results showed that the outside surface of the zeolite nanobox is clean (i.e., no Pt nanoparticles on the surface).

## **POSTERS AND PRESENTATIONS**

- A. Farghaly, N. Kariuki, and D. Myers, "Fuel Cell Catalysts Encased in 1D and 3D Porous Frameworks", 235<sup>th</sup> Electrochemical Society Meeting, Dallas, TX, May, 2019.
- A. Farghaly and D. Myers, "Sol-Gel Assisted Synthesis of Encased Polymer Electrolyte Fuel Cell Cathode Catalysts", 236<sup>th</sup> Electrochemical Society Meeting, Atlanta, GA, October, 2019.

