
Lab Call FY19: Polymer Electrolyte Fuel Cell Electrode Structures with Encased Catalysts to Eliminate Ionomer Adsorption on Catalytic Sites

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Subcontractors:

- Oak Ridge National Laboratory, Oak Ridge, TN
- National Renewable Energy Laboratory, Golden, CO

Project Start Date: October 1, 2019
Project End Date: September 30, 2020

Overall Objectives

The overall objective of this project is to improve the high current density hydrogen-air performance of polymer electrolyte fuel cells (PEFCs) having Pt loadings of 0.125 mg_{Pt}/cm² versus the state-of-the-art PEFCs that use carbon-supported Pt or Pt_xCo_{1-x} catalysts, while also maintaining the performance over the 8,000 h operating time target.

- Address the lack of sufficient areal power density at rated power for an automotive PEFC stack.
- Address 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.

Fiscal Year (FY) 2019 Objectives

- Incorporate Pt and Pt_xCo_{1-x} nanoparticles into the cages of commercial zeolites and determine maximum metal loadings.
- Achieve oxygen reduction reaction (ORR) activities in thin-film rotating disk electrode (TF-RDE) tests of >0.2 A/mg_{Pt}.
- Develop synthetic methods to increase metal loading in zeolite cages and to enhance catalyst electronic conductivity.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- A. Electrode Performance
- B. Cost
- C. Durability.

Technical Targets

This project aims to improve the high current density hydrogen-air performance of PEFCs having Pt loadings of 0.125 mg-Pt/cm² versus the state-of-the-art PEFCs that use carbon-supported Pt or Pt_xCo_{1-x} catalysts, while also maintaining the performance over the 8,000 h operating time target to achieve the following goals:

- Performance: >300 mA/cm² at 800 mV; >1,000 mW/cm² at rated power (150 kPa, 94°C, >0.67 V)
- Cost: 8 kW/g_{PGM}, <\$40 kWe system (<\$20 kWe net stack), <0.125 mg_{PGM}/cm²
- Durability: <40% loss in cathode mass activity, <30 mV loss at 0.8 A/cm², and <30 mV loss at 1.5 A/cm² after catalyst and support accelerated stress tests, respectively.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

FY 2019 Accomplishments

- Synthesized 62 Pt-based catalysts by incipient wetness/ion-exchange using a cationic Pt complex and two zeolite types (ZSM-5² and mordenite) and targeting three Pt loadings: 1, 5, and 10 wt %.
- Achieved 284 mA/mg_{Pt} ORR mass activity for Pt/ZSM-5, as measured using the TF-RDE technique.
- Synthesized ~300-nm-diameter ZSM-5 crystals with incorporation of Pt₃Co at 20 wt % target loading.
- Developed a synthetic route for forming hollow zeolite nanocrystals with porous walls (0.5 nm pore size) and encased ~5 nm Pt nanoparticles exclusively inside the nanocrystals.
- Developed a method to impart electronic conductivity to the zeolites through carbon deposition.

INTRODUCTION

While the catalytic activity of numerous Pt-based, carbon-supported PEFC cathode catalysts far exceed the DOE Office of Energy Efficiency and Renewable Energy Fuel Cell Technologies Office ORR activity targets, at the low cathode loadings necessary to achieve the stack cost targets (<0.1 mg-Pt/cm²) the cathode performance at high current densities (>1 A/cm²) is lower than expected based on kinetic losses. While not completely understood, the voltage losses at high current densities appear to scale with the available electrochemically active surface area (ECA) of the catalyst and to be associated with a phenomenon local to the catalyst surface and with interactions between the perfluorosulfonic acid (PFSA) ionomer and the catalyst surface [1]. It has been proposed that the ionomer is forming a thin film coating the catalyst particles and that this thin film or its interface with the catalyst has a high resistance to oxygen transport [1]. In addition to transport losses, it has been shown that PFSA does significantly inhibit ORR kinetics [2, 3].

The primary source of PEFC performance loss with load cycling for PEFCs containing dispersed, carbon-supported catalysts is loss of Pt ECA due to Pt particle migration and coalescence on the carbon support, Pt dissolution from smaller particles in distribution, followed by re-deposition on larger particles or loss from the electrode [4, 5], and, additionally, leaching of the ORR activity-enhancing alloying element (e.g., Co or Ni) from Pt alloy catalysts [6, 7]. Another source of cathode performance loss, especially prevalent when the cathode experiences high voltages during cell start-up and shut-down, is corrosion of the carbon support at the interface between the catalyst particle and the support, resulting in loss of electrical connection to the particles and to loss of electrode porosity [8, 9].

APPROACH

In this project we intend to address the issues of ionomer poisoning of ORR activity, local oxygen transport resistance, and the lack of cathode performance durability by encasing the Pt and Pt_xCo_{1-x} alloy catalyst particles in the cavity of a zeolite. The microporous zeolite cages will exclude ionomer but allow passage of oxygen, water, proton, and electrons to and from the catalyst particles inside the cages. Encasing the catalyst particles will not only eliminate the poisoning and transport issues related to direct contact between the PFSA and catalyst surface, it will also prevent loss of catalyst ECA resulting from particle migration and coalescence and carbon corrosion-related degradation by eliminating direct contact between corrosion-catalyzing catalyst nanoparticles and carbon. This approach is also expected to decrease Pt dissolution-related surface area loss and ORR mass activity loss due to leaching of cobalt from the alloy particles by decreasing the acidity (i.e., increasing the pH) of the environment around the catalyst particles.

Zeolites are alumino-silicates that form ordered structures with well-defined channels and cavities. Zeolites' ability to "size sort" molecules arises from these well-defined channels that allow passage of molecules with diameters smaller than the channel diameters but exclude larger species from the interior of the zeolite. Encapsulation of catalytic particles inside zeolites has also been widely used in the gas-phase catalysis industry to prevent particle sintering and loss of catalyst surface area under the elevated temperature reaction conditions [10]. The molecular diameter of oxygen is 3.46 Å [11], and PFSA forms rod-like particles with diameters of

² Zeolite Socony Mobil-R, an aluminosilicate zeolite with the chemical formula Na_nAl_nSi_{96-n}O₁₉₂·16 H₂O (0<n<27)

approximately 2.0–2.5 nm in the solutions used to make PEFC electrodes [12]. The proposed approach, encasing the ORR catalyst in a zeolite, relies on this difference in molecular diameters to allow access of oxygen to the catalyst surface through the zeolite channels while preventing ionomer access. In addition to discriminating between oxygen and PFSA, the zeolite cages must also have sufficient proton and electronic conductivity to the interior of the cage to provide these species for the ORR, and they must be stable in the acidic and oxidizing environment of the PEFC cathode. While zeolites are proton conductors by virtue of their substitution of trivalent aluminum for divalent silicon [13], zeolites have very low electronic conductivity. We have been initially addressing this issue by forming a composite of the catalyzed zeolite and high-surface-area carbon but are also developing methods to form thin porous carbon shells around the catalyzed zeolites and growing graphene-like carbon within the micropores of the catalyzed zeolites.

RESULTS

Sixty-two unique Pt/zeolite samples with target Pt loadings of 1, 5 and 10 wt % were synthesized using commercial zeolites, mainly ZSM-5. The ORR activity of these catalysts was screened using the TF-RDE technique and Pt/zeolite ORR activity of >0.2 A/mg-Pt was achieved. Transmission electron microscopy (TEM) characterization of several of the Pt/commercial ZSM-5 samples prepared via different routes showed that the Pt nanoparticles were deposited both inside the zeolite cavities and on the surface of the zeolites, as depicted in Figure 1. In addition, the commercial zeolites are of micron size and have irregular shapes. This morphology is not ideal for effective utilization in the cathode catalyst layer of a membrane-electrode assembly where small uniform particle/aggregate sizes that are easily dispersed in ionomer are needed. Another challenge with the commercial zeolites and zeolites in general is their low electronic conductivity.

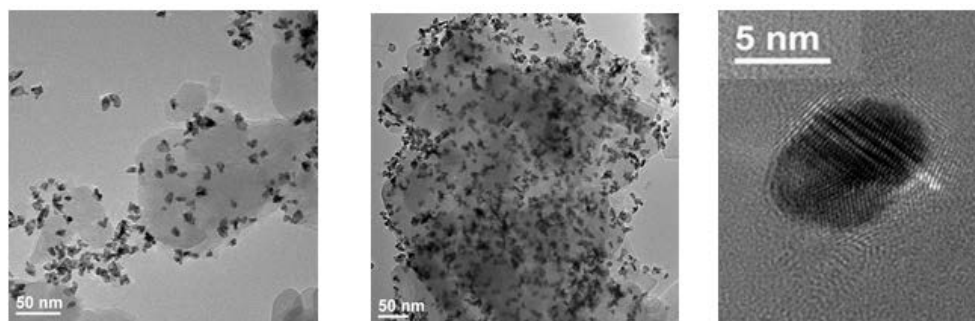


Figure 1. TEM micrographs of Pt/commercial ZSM-5 catalysts prepared in this project showing that Pt nanoparticles are deposited both inside the zeolite cavities and on the surface of the zeolites

To address these challenges, we developed methods to synthesize well-defined zeolite nanocrystals with diameters of 80 nm and 300 nm (Figure 2). We were able to load the 300-nm-diameter zeolite with 20 wt % Pt_3Co . We also developed synthetic routes for forming hollow zeolite nanocrystals and encasing Pt nanoparticles inside the zeolite cavity (Figure 3). These hollow nanostructures, which comprise a porous zeolitic shell with 0.5 nm pore size, guarantee effective separation between the ionomer aggregates with ~ 5 nm diameter and the platinum nanoparticles encased in the nanostructures. The ORR activity of the Pt@nano-zeolite catalyst was determined by the TF-RDE technique. The catalyst was found to be active for the ORR but limited by electronic conductivity. Incorporation of either Vulcan or Ketjen carbon in the catalytic layer on the RDE mitigated the conductivity issue but resulted in oxygen diffusion limitation through the film due to its excessive thickness from the carbon component. Fuel cell testing of the Pt@nano-zeolite/carbon/ionomer composite also exhibited mass transport limitations.

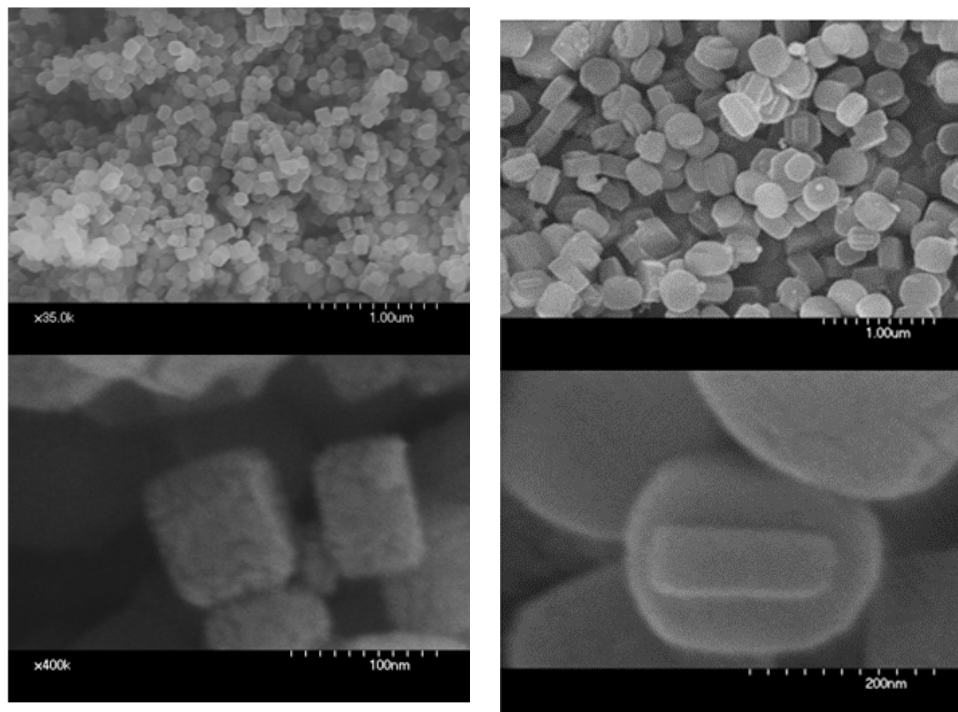


Figure 2. (Left) Scanning electron microscopy (SEM) micrographs of nanocrystals of ZSM-5. The dimensions of the nanocrystals are 80 nm across a side. (Right) SEM micrographs of ~300-nm-diameter ZSM-5 crystals with 20 wt % Pt₃Co loading.

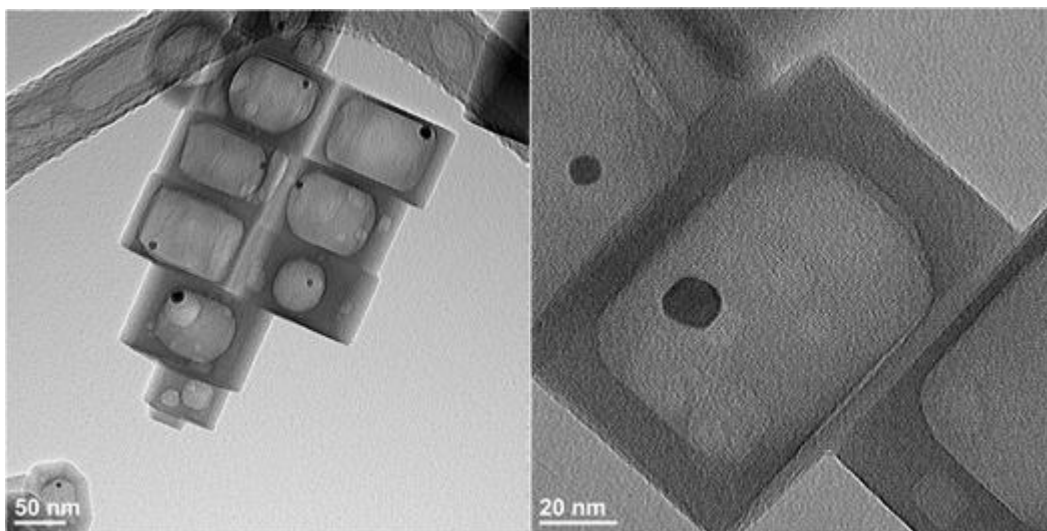


Figure 3. TEM images of the Pt@ZSM-5 hollow nanocrystals. Single platinum nanoparticles of ~5–10 nm diameter (darker spots inside rectangular grey zeolites) are encased inside the hollow ZSM-5 nanocrystals.

To address the issue of low electronic conductivity of the Pt@nano-zeolite, we have been exploring ways to incorporate graphitic carbon into the nano-zeolite cages resulting in a Pt particle protected by a porous graphitic shell. We have developed a synthetic method and successfully synthesized a zeolite nanocrystal that showed high electronic conductivity in RDE tests.

CONCLUSIONS AND UPCOMING ACTIVITIES

To prove the concept of protecting Pt nanoparticle PEFC cathode catalysts from the detrimental consequences of direct interaction with the PFSA ionomer, numerous samples were made with the goal of incorporating Pt and Pt_xCo_{1-x} nanoparticles inside the cages of commercial zeolites. TEM characterization of these samples showed that, without exception, Pt particles were deposited both inside the zeolite cavities and on the surface of the zeolites. In addition, the commercial zeolites were not homogeneous in size or shape. Methods were developed in this project to synthesize nanocrystals of ZSM-5 with uniform particle size and shape and to form zeolites with hollow cavities for incorporation of Pt nanoparticles. Methods have also been developed to deposit/grow graphene-like carbon within the micropores of the nanocrystals to impart electronic conductivity to the zeolites. These synthesis methods are currently being scaled up and, in the near future, zeolite-encapsulated Pt₃Co will be incorporated into membrane-electrode assemblies and its performance and durability tested at the National Renewable Energy Laboratory.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. A.A. Farghaly, N.N. Kariuki, and D.J. Myers, "Fuel Cell Catalysts Encased in 1D and 3D Porous Frameworks," 235th Electrochemical Society Meeting, Dallas, TX, May 29, 2019.
2. A.A. Farghaly and D.J. Myers, "Sol-Gel Assisted Synthesis of Encased Polymer Electrolyte Fuel Cell Cathode Catalysts," 236th Electrochemical Society Meeting, Atlanta, GA, October 13, 2019.

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