V.C.2 Rationally Designed Catalyst Layers for PEMFC Performance Optimization

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Overall Objectives

Realize the oxygen reduction reaction (ORR) mass activity benefits of advanced Pt alloy cathode electrocatalysts observed at low current densities and on oxygen and in rotating-disk electrode (RDE) measurements in membrane electrode assemblies (MEAs) and stacks operating at high current densities (>1 A/cm²) and on air.

Fiscal Year (FY) 2013 Objectives

- Identify the sources of the performance loss of cathodes based on an advanced cathode catalyst.

- Establish the correlations between agglomerate structure in the advanced cathode catalyst and platinum catalyst inks and electrode layer structure using, for example, X-ray and microscopic techniques.

- Determine the effects of ink composition (e.g., catalyst to ionomer ratio) and catalyst type (i.e., advanced alloy versus Pt of similar particle size) on electrode properties and performance.

- Develop a method and an algorithm to map electrode structure from imaging data.

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 Plan:

(C) Performance

(B) Cost

(A) Durability

Technical Targets

Meeting the project objectives will enable proton exchange membrane fuel cells (PEMFCs) to achieve the DOE 2017 fuel cell technical targets:

- Performance: >300 mA/cm² at 800 mV and >1,000 mW/cm² at rated power

- Cost: $5-9/kWe catalyst and <$30 kWe system

- Durability with cycling: 5,000 hours (<80ºC) and 2,000 hours (>80ºC), <40% loss of initial catalytic mass activity at 900 mV on O_2; <30 mV loss at 0.8 A/cm²

FY 2013 Accomplishments

- Identified advanced cathode catalyst to be studied in this project. Synthesis of this catalyst has been scaled up to hundred gram quantities.

- Performed ultra-small angle X-ray scattering (USAXS) and cryogenic transmission electron microscopy (TEM) on catalyst-ionomer-solvent inks containing the advanced alloy catalyst, a standard Pt/C, and Pt/C with particle size comparable to that of the advanced alloy catalyst to determine the catalyst and ionomer primary particle and agglomerate size and size distribution.

- Developed a Monte-Carlo simulation model to determine the structure of the catalyst layer knowing the catalyst ink composition with inputs of the size distributions of Pt or alloy particles, primary carbon particles and carbon agglomerates, and primary ionomer and ionomer agglomerates being determined using USAXS and TEM.

- Fabricated catalyst-coated membranes containing the advanced alloy catalyst and platinum catalysts of two particle sizes and initiated electrochemical measurements to determine the sources of voltage losses.

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INTRODUCTION

One of the major cost contributors to PEMFC systems for automotive and stationary power applications is the platinum-group metal (PGM) cathode electrocatalyst [1]. The high cost of the cathode electrocatalyst results from the high loadings of catalyst necessary to overcome the limitations of low ORR activity, low utilization of PGM, and loss of activity with operating time. Alloying platinum with base metals (e.g., cobalt, iron, and nickel) is well-known to improve its intrinsic ORR activity [2]. While ORR activities exceeding the DOE 2017 targets (>0.44 A/mg PGM and 720 µA/cm² @ 900 mV) have been demonstrated for high-surface-area-carbon-supported Pt alloy and core-shell nanoparticle catalysts in aqueous cell RDE tests [3], some as high as 2 A/mg Pt [4], the full activities and performance of these promising catalysts have yet to be achieved in MEAs, especially when operating at realistic current densities and on air rather than oxygen. Figure 1 illustrates that PEMFC cathodes containing alloy catalysts outperform cathodes containing Pt catalysts at all current densities when operating with oxygen as the cathode gas and at current densities <1,000 mA/cm² when operating with air as the cathode gas.

There are several possible reasons the full potentials of the advanced alloy, de-alloyed, and core-shell materials have not been realized in MEAs operating on air and at current densities >1 A/cm^2. One may arise from the complex requirements for full utilization of the electrocatalytic sites and for adequate reactant transport in the MEA cathode layer. These requirements are easily fulfilled in the RDE environment by virtue of the thinness of the catalysts film, its intimate contact with a glassy carbon substrate, flooding of the film with an oxygen-saturated proton-conducting electrolyte, and efficient transport of reactants to the film by electrode rotation. These requirements are also easily
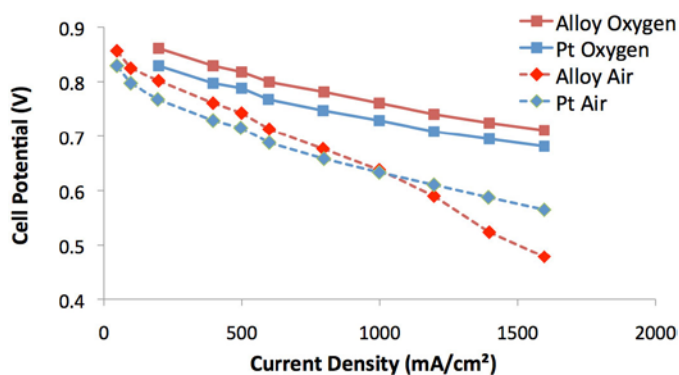
met in the fuel cell at low current densities in an oxygen environment where the electrocatalytic reaction rate dominates the voltage losses and demands on transport to the reactive sites are easily filled. Fulfillment of these requirements at high current densities in an MEA cathode relies on optimization of the electrode composition and structure to balance the structure of the proton-conducting phase, the electron-conducting phase, and the distribution and size of pores for reactant/product diffusion. This optimization is a lengthy, trial-and-error process and has taken several years for the traditional Pt-only cathode layers. The goal of this project is to optimize the electrode layer composition, structure, and materials properties of cathodes based on advanced alloy cathodes so they can achieve their entitled performance at high current densities and on air and exceed the DOE performance and durability targets for PEMFCs for automotive applications.

APPROACH

This project is following a new and comprehensive approach to achieving the goals: (1) determination of the agglomerate, particle, and pore structure of the advanced Pt alloy/C-based electrodes; (2) using this information and electrochemical diagnostic techniques to determine the performance-limiting property of the current electrode structure; (3) rational design of the catalyst layer/MEA structure guided by computational modeling; (4) development of the catalyst support morphology, surface functionality, and catalyst ink composition to be used for making the performance-optimizing cathode layer, guided by the modeling results; (5) study of the dispersion of Pt alloy/C catalyst aggregates and the perfluorosulfonic acid ionomer particles in liquid media and the agglomeration of these aggregates/particles during the evaporation process; and (6) development of a solvent removal process that maintains the dispersion and agglomerate structure of the ink.

The advanced Pt alloy is a state-of-the-art de-alloyed Pt/Ni catalyst developed in the on-going General Motors-led project entitled "High-Activity Dealloyed Catalysts." The key characteristics and metrics of this catalyst are:

- Catalyst deposited as nanoparticles onto conventional carbon black supports, identical to those used for standard Pt/C reference catalysts.

- Catalyst deposition chemistry is proven and via methods scalable to commercial levels.

- Nominal initial atomic composition prior to de-alloying is $Pt_{25}Ni_{75}$.

- Mass activity (O_2 @ 0.9 V) is >0.60 A/mg Pt (exceeds DOE 2017 target).

- Mass activity loss after 30,000 0.60 to 1.0 V cycles is <40% (exceeds DOE kinetic stability target).

FIGURE 1. Example of lack of performance benefit of a Pt alloy over Pt when operating at >1,000 mA/cm² on air (cathode loading 0.2 mg Pt/cm², 80°C, 50/50 kPa gauge).

RESULTS

The advanced cathode catalyst to be studied in this project has been identified. It has oxygen reduction activity and kinetic stability in an MEA that exceeds DOE 2017 target and has been scaled up by Johnson Matthey Fuel Cells. USAXS and TEM have been performed on catalyst-ionomer-solvent inks. These inks contain the standard Pt/C catalyst (Pt particle size of 2-3 nm), a Pt/C catalyst that has been heat-treated to grow the particle size to be comparable to that of the advanced alloy catalyst (>5 nm), or the advanced alloy catalyst. The ionomer to catalyst ratio and type and amount of solvent used in the inks was varied to determine how they affect the ink and electrode layer structure and, ultimately, performance. Analysis of these USAXS and TEM data is providing the ionomer and catalyst/carbon primary and agglomerate structure in the ink. A Monte Carlo simulation model has been developed to determine the structure of the catalyst layer knowing the catalyst ink composition. The model inputs include the size distributions of Pt particles, primary carbon particles and carbon agglomerates, and primary ionomer particles and ionomer agglomerates, as determined from the USAXS and TEM measurements. Catalyst-coated membranes using the advanced alloy catalyst in the cathode layer and platinum catalysts, for comparison, have been fabricated by Johnson Matthey Technology Center and are now being tested at United Technologies Research Center to determine their overall performance and the sources of voltage losses using a variety of electrochemical techniques, such as electrochemical impedance spectroscopy and limiting current using a variety of cathode gas compositions.

CONCLUSIONS AND FUTURE DIRECTIONS

As this project is relatively new, no major conclusions are available at this point. Future directions will be to determine the sources of the voltage losses that are unique to the advanced alloy catalysts operating at high current densities and on air and to mitigate these losses. The approaches to mitigating these losses will be to alter the catalyst layer structure and composition and the intrinsic materials properties, such as proton conductivity of the carbon support. Other approaches will be developed, if necessary, when the sources of these voltage losses are known.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Myers, D., "Rationally Designed Catalyst Layers for PEMFC Performance Optimization", 2013 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Washington D.C., May 13–17, 2013. (Poster)

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