
V.D.20 Instability of Noble Metal Catalysts in Proton Exchange Membrane Fuel Cells: Experiments and Theory

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Abstract

In this study, we argue that increasing Pt nanoparticle sizes from 2-3 nm and 4-5 nm can significantly increase the stability of these particles against dissolution and coarsening. We show that the stability of Pt/C nanoparticles upon voltage cycling is enhanced by heat-treatments, which is attributed to eliminating Pt nanoparticles smaller than 2 nm and increasing the mean particle size to ~4 nm. In addition, we demonstrate that the particle size distribution has a large impact on the rate of surface area of Pt during cycling. A narrow distribution of Pt nanoparticles provides better stability against coarsening via Ostwald ripening.

Progress Report

When the cathode is exposed to voltages higher than 0.8 V vs. RHE (steady-state or transient), where the solubility of Pt nanoparticles can be significant, the surface area loss in the fuel cell cathode can be dominated by Pt loss from carbon support and coarsening of Pt nanoparticles. Pt loss from carbon support can result from reduction of soluble species and precipitation of Pt crystals in the ionomer phase, which has been studied in detail in our previous work [1-7]. *Coarsening* of individual Pt nanoparticles on carbon may involve dissolution of Pt from small particles, diffusion of soluble Pt species from small to large particles in the ionomer phase and redeposition/reduction of soluble Pt species onto large particles on the nanometer-scale. This process is analogous to the Ostwald ripening process that typically involves transport of atoms or molecules from small particles to large particles and growth of large particles at the expense of small ones, driven by reduction in the surface energy. Both Pt particle size and size distributions can have a significant impact on the solubility and coarsening of Pt nanoparticles and we here examine their effects on the surface loss using combined experimental and computational studies.

Gibbs-Thomson and the Stability of Heat-Treated Pt Nanoparticles Upon Voltage Cycling - Given the stability implications of the Gibbs-Thomson equation, one expects that increasing Pt particle sizes and decreasing the number of particles smaller than 2 nm would significantly enhance stability. Recently Makharia *et al.* have reported that the stability of Pt nanoparticles upon potential cycling in PEM fuel cells can be improved by heat-treatments at high-temperatures [7]. However, the mechanism by which the stability was obtained nor the heat-treatment condition was reported. Heat-treatments

Objectives

In this project, we probe the nature of Pt coarsening in Pt/C electrodes in a PEM fuel cell and an acid environment through combined controlled experimental approaches and modeling at different length scales. The aim of this work is to determine key physical parameters that govern Pt surface area loss, and develop predictive kinetic models for activity loss in PEM fuel cell electrodes.

Technical Barriers

The estimated cost of PEM fuel cell systems for automotive applications is significantly higher than existing, internal combustion technologies (~\$35/kW for advanced technologies) and the lifetime of PEM fuel cell systems is limited to 2,000 hours, significantly shorter than the required 5,500 hours of operation in a vehicle. The instability of noble metal catalysts in fuel cell electrodes significantly decreases the availability of TPB regions and increases the activation overpotential for oxygen reduction, which limits the cost, energy conversion efficiency and lifetime of current proton exchange membrane (PEM) fuel cell systems. Mechanisms of surface area loss of supported Pt nanoparticles carbon in contact with an ion-conducting phase at temperatures lower than 200°C are not understood, which is essential to develop durable Pt and Pt-M alloy nanoparticles on carbon meet the required lifetime and efficiency of PEM fuel cells.

at high temperatures can increase particle sizes and decrease the number of small Pt nanoparticles by crystal migration. Here we describe a recent experiment that demonstrates the connection between changes in Pt particle size through heat treatments and reduced Pt surface area loss and enhanced Pt stability during potential cycling in acid.

We here examine three Pt/C samples: pristine TTK 28 wt%, and two heat-treated samples at 900°C in Ar for one minute (HT-1) and 15 minutes (HT-2). The histograms of these three samples are compared in Figure 1, where Pt particle sizes increase upon heat-treatments. It is interesting to note that the fraction of Pt particles in the range of 1-2 nm is reduced considerably upon heat-treatments, which can be seen clearly in Figure 1. Small Pt particles may migrate on the carbon support, join with other particles and coalesce into large particles during the heat-treatment. These three samples were then cycled from 0.6 V to 1.0 V vs. RHE in 0.5M H₂SO₄ at a scanning rate of 20 mV/s at 23°C.

Heat-treated samples show much reduced Pt surface area loss and improved stability upon potential cycling, as shown in Figure 2, which results from loss of Pt by dissolution, and growth of Pt nanoparticles by dissolution and redeposition (Ostwald ripening). It is hypothesized that heat-treated samples having lower fractions of Pt nanoparticles smaller than 2 nm relative to the pristine sample have reduced Pt solubility, which reduces Pt loss and surface area loss upon voltage cycling. As no significant change in the Pt particle size before and after voltage cycling was noted in the HT-2 sample, it is believed that the surface area loss shown in Figure 2 largely result from Pt dissolution. In addition, the rate of surface loss in the first 400 cycles is markedly reduced in the heat-treated samples. It is proposed that the rapid surface area loss of Pt nanoparticles in the pristine sample upon initial potential cycling largely results from rapid dissolution of small Pt nanoparticles of 1-2 nm into the acid solution. This is in good agreement with experimental TEM observations that most small Pt particles disappeared in the pristine Pt/C sample after potential cycling, as shown in the histograms of Pt particles before and after voltage cycling. These experimental observations support the concept of the dramatically decreased stability of particles in the 1-2 nm region associated with the Gibbs-Thomson effect.

The Electrochemical Surface Area Loss Model:

The goal of the model development is to simulate the degradation of electrochemically active surface area of carbon supported Pt nanoparticle catalysts under fuel cell conditions. The motivation is both to improve understanding of which factors dominate surface area loss and suggest how changes in catalyst design could enhance long-term stability. The model has been developed as an extension of the work of Darling and

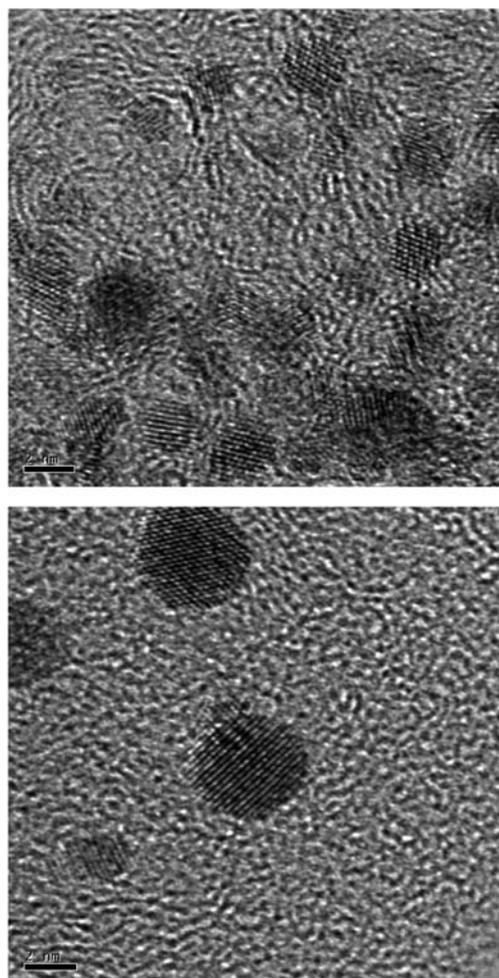
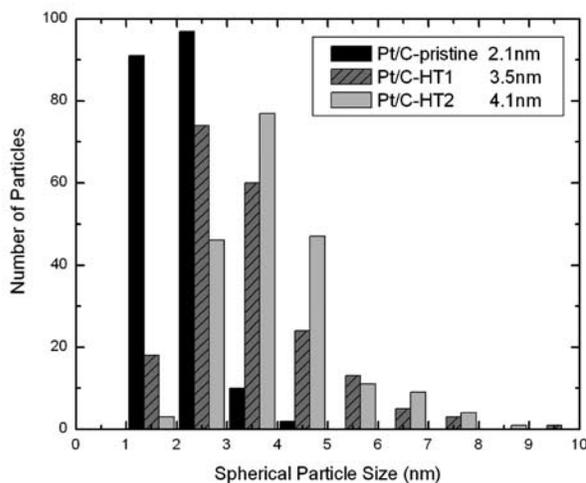


FIGURE 1. Top: Histograms of pristine, Pt/C-HT1 and Pt/C-HT2 samples; center: HRTEM image of the Pristine; bottom: HRTEM image of the Pt/C-HT1.

Meyers [3,4]. We have added the process of hydrogen induced precipitation to their original model, which included processes of dissolution and oxidation. The

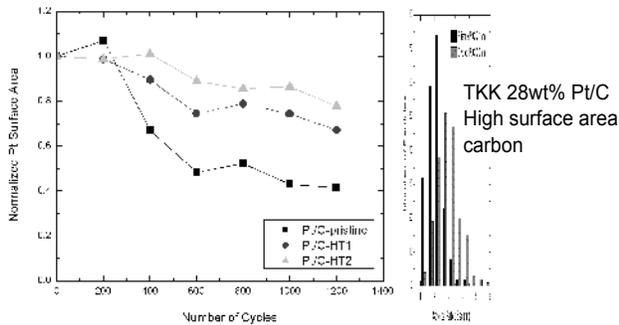


FIGURE 2. Left: Degradation of electrochemical surface area of Pt nanoparticles of the three samples with the number of cycles. Cycled in 0.5M H₂SO₄, between 600 mV and 1000 mV (vs. RHE) for 1,200 scans at 80°C. Right: the histograms of the pristine sample before and after voltage cycling.

new model therefore include the following fundamental processes

1. Pt dissolution: $Pt_{(s)} \leftrightarrow Pt^{2+}_{(aq)} + 2e^{-}$
2. Pt oxidation: $PtO_{(s)} + 2H^{+} + 2e^{-}$
3. Pt oxide dissolution: $PtO_{(s)} + 2H^{+} \leftrightarrow Pt^{2+}_{(aq)} + H_2O$
4. H₂ induced Pt precipitation: $Pt^{2+}_{(aq)} + H_2 \leftrightarrow Pt_{(s)} + 2H^{+}$

The physical structure and active processes for the model are shown schematically in Figure 3. Chemical and electrochemical rate equations for processes 1-3 above were adapted from Darling and Meyers, although the parameters describing oxide-Pt interaction had to be refit to their experimental cyclic voltammetry curves to give accurate data. Diffusion through the ionomer to the crossover H₂ was added to the original model. Initial simulations have focused on modeling the effects of particle size distribution. We have demonstrated an unexpected dependence of surface area loss on the shape of the particle size distribution, beyond a simple dependence on average diameter.

Particle Size Distribution Effects: While it is generally recognized that particle size may play a significant role, the possible influence of the shape of the particle size distribution on the loss of Pt surface area has largely been ignored. Three different particle size distributions are considered, ranging from Uniform, to Gaussian, to a sharp Delta function, all of which have the same loading (0.4 mg/cm²) and the same specific

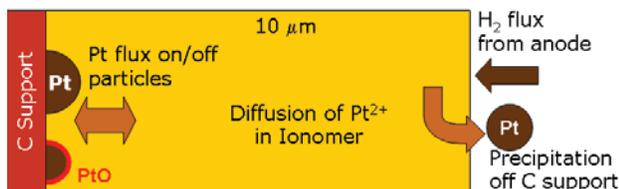


FIGURE 3. Schematic Picture of Model Geometry and Processes

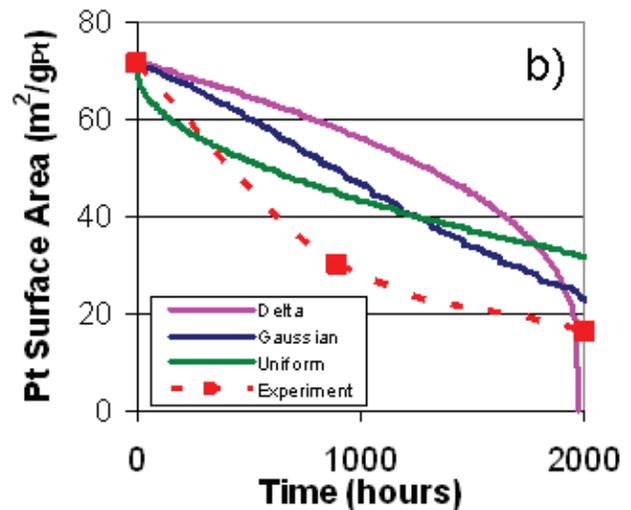
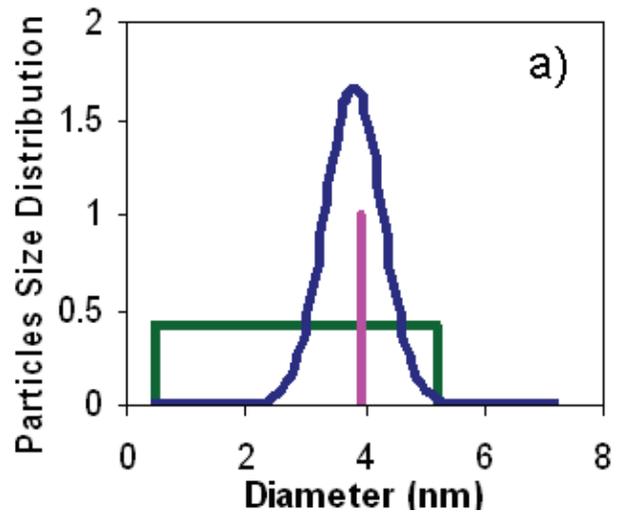


FIGURE 4. a) Uniform, Gaussian, and Delta function type particle size distributions and b) simulations of their respective surface area loss at 0.95 V.

surface area of about 72 m²/g (shown in Figure 4a). The model is used to simulate the loss of Pt surface area as a function of time for 2,000 h at constant 0.95 V (OCV) potential under 5 mA/cm² of H₂ crossover. The results are shown, along with experimental data from Ferreira et al. [1], in Figure 4b. Deviations from the experimental data are likely due to different particle size distributions and the presence of some carbon corrosion in the experiment. The results demonstrate the shape and total amounts of surface area loss are strongly dependent on the particle size distribution, even for distributions corresponding to identical loading, surface area, and similar mean diameters. The Uniform distribution, because of its weighting toward less stable smaller particles, shows the fastest initial surface area loss. While the Delta distribution decays more slowly at first, at later times it has no tail of larger particles to keep it stable and it shows complete and rather sharp

total dissolution. The Gaussian distribution, perhaps the most realistic, generally sits between the Uniform and Delta extremes. Interestingly, although the Uniform distribution has the smallest mean diameter (only 3.4 nm), it shows the best long-term stability. *This clearly demonstrates that the shape of the particle size distribution, not just its mean diameter, is essential to understanding and controlling stability.*

Future Work: In our experimental efforts, we will study 1) surface facet effects on the instability of Pt nanoparticles and 2) the stability of PtM alloy catalysts during voltage cycling. In our computational side, we are extending the model to include crystal migration and coalescence, likely to be dominant at lower potentials and carbon corrosion effects will be incorporated based on the kinetic model of Makharia et al. [7]. These steps will allow the model to treat all significant loss mechanisms, at which point more detailed studies of temperature, voltage cycling, particle size distribution, and oxidation effects will be undertaken.

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