Preparation and Characterization of Novel Platinum-on-Carbon Catalysts with Controlled Cluster Size for Application in PEM Fuel Cells

E.N. Coker,[1] W.A. Steen,[1] J.E. Miller,[1] A.J. Kropf,[2] J.T. Miller[3]

[1]Sandia National Laboratories, Albuquerque, NM, U.S.A.;
[2]Argonne National Laboratory, Argonne, IL, U.S.A.;   [3]BP Corporation, Naperville, IL, U.S.A.

Introduction

State-of-the-art electrocatalysts for Polymer Electrolyte Membrane Fuel Cells (PEM-FCs) rely on large quantities of platinum to achieve acceptable performance [1]. This presents a significant hurdle to hydrogen FC-powered vehicles; a commercially viable electrocatalyst will require almost an order-of-magnitude reduction in Pt usage to meet both cost and Pt availability constraints. One avenue to achieve this reduction is through optimization of Pt cluster sizes for maximum electrochemical activity per unit mass. However, the interplay between maximizing Pt dispersion and size-specific reactivity needs to be better understood. The physical and chemical properties of nanoparticles of various elements are extremely sensitive to the number of atoms comprising the cluster when they contain less than a few dozen atoms. Furthermore, these variations in properties are often manifested in a non-linear fashion as the size of the cluster changes [2], and may be attributed to electronic and/or structural changes. Also the interaction of small clusters of atoms with the surface of a support may result in alteration of the electronic state of the cluster, depending on the nature of the support material [3]. There is some evidence that as the Pt cluster size is reduced below ~3nm, the specific electrochemical activity (per unit mass) diminishes due to changes in cluster structure [4], however, large uncertainties exist due to the broad size distributions of most catalyst preparations analyzed in the literature. Direct measurement of the size-dependent properties of small Pt clusters with narrow size distribution would clarify the issue of size-dependent properties and enable design of optimized electrocatalysts for PEM-FCs.

Zeolites play host to noble metal clusters for numerous catalytic applications [5], and well-defined clusters of narrow size distribution down to ~1nm have been obtained under suitable conditions [6,7]. However, due to their insulating characteristics, zeolite-supported clusters are not suitable as electrocatalysts. We have developed procedures whereby size-controlled Pt clusters in a zeolite could be rendered electrocatalytically active. These materials should provide the means to develop a clear understanding of the size-specific electrochemical properties of small Pt clusters, enabling development of enhanced PEM-FC electrocatalysts.

Methods and Materials

These materials are referred to as [m]PtX(n:t), where m is the Pt-loading in wt.-% (anhydrous, de-ammoniated basis) and n and t are the calcination heating rate in °C min^{-1} and the final calcination temperature in °C, respectively.

The [m]PtX(n:t), Pt/C, and intermediate materials have been characterized using a variety of techniques, including TEM, XRD, EXAFS, BET Surface Area analysis, chemisorption, thermo-gravimetric analysis (TGA) and ^{13}C MAS-NMR.

Results

Analysis by XRD and TEM revealed a strong dependence of Pt cluster size on calcination temperature, ramp rate, and sample hydration. For instance, [20]PtX(2:400) possessed large particles of Pt ~3-6nm in diameter and clearly identifiable by XRD, while the Pt clusters in [20]PtX(1:400) were too small to diffract X-rays coherently (~0.8 – 1.2 nm). Evacuation of samples at room temperature to reduce the level of hydration prior to calcination resulted in a reduced dependence on ramp rate, and an overall reduction in cluster size compared to fully hydrated samples undergoing identical calcination treatments. Fig. 1 shows TEM images of two samples, A: [20]PtX(0.1:350), and B: [5]PtX(0.1:350), both calcined at 0.1°C min^{-1}, but with differing Pt loadings. Both samples exhibit almost exclusively sub-nm clusters, virtually indistinguishable by TEM. However, EXAFS analysis of these samples in their reduced state yielded Pt-Pt coordination numbers (CN) of 7.7 ([20]PtX(0.1:350)) and 6.1 ([5]PtX(0.1:350)), indicating a reduction in cluster size with lower Pt loading. These average, bulk CN values are likely skewed upward due to a small number of larger (2-4nm) clusters (identified from TEM images of [m]PtX(n:t), some of which can be seen in Fig 1); methods are being developed to reduce the occurrence of such large particles. Results of EXAFS analysis of [5]PtX(0.1:350) (similar to sample in Fig. 1B) are given in Figs. 2 and 3. TEM images indicate that this material possessed a relatively low density of large Pt particles (~2-4nm). Pt-Pt CN = 6.0 for this material in the fully reduced state (Fig. 2, and the blue curve in Fig. 3). The material in the reduced state is compared to the as-synthesized, calcined material (fully oxidized, the red curve in Fig. 3; 30% Pt^{2+}, 70% Pt^{4+}), as well as the reduced material after it was exposed to ambient air for ~ 5 minutes (during which rapid re-oxidation of the Pt surface occurred, green curve in Fig. 3; 60% Pt^{0}, 40% Pt^{4+}).

After infiltration and polymerization of FFA, pyrolysis of [20]PtX(0.1:350)/p-FFA at 600°C (to produce [20]PtX(0.1:350)/C) resulted in only minor sintering of the Pt clusters to ~0.7-1.2nm, whereas identical heat-treatment of [20]PtX(0.1:350) resulted in doubling of the cluster diameter, as evidenced by TEM. ^{13}C MAS NMR has shown a transition from mostly sp^{3} carbon in the polymer-containing Pt-zeolite to mostly sp^{2} in the pyrolyzed material, in agreement with the formation of graphitic sheets.

Acid washing of [m]PtX(n:t)/C to remove the zeolite host resulted in negligible loss of Pt, while in some cases, residual Si and Al from the zeolite were detected in the catalyst (Pt/C) by elemental analysis. Initial electrochemical tests indicated that the platinum in these samples was electroactive, and that the carbon matrix was conductive [8]. Mean cluster sizes for Pt/C calculated through adsorption methods (H$_2$- and CO-chemisorption, CO-stripping voltammetry) were consistently larger than those measured by TEM and EXAFS [9].
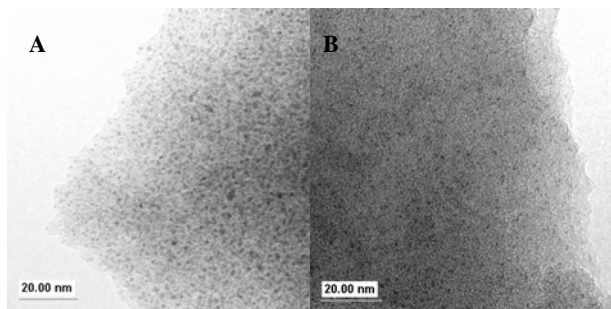
Figure 1. TEM images of Pt clusters (dark spots) in zeolite X. A: [20]PtX(0.1:350); B: [5]PtX(0.1:350).

Discussion

The dependence of cluster size on calcination ramp rate may be understood on the basis of strong adsorption of water and ammonia in the zeolite. Because the residence time of these adsorbates within the zeolite channels can be very long (depending on the hydrophilicity of the particular formulation), a slow heating rate can be beneficial to reducing sintering of particles, since it is the hydrated and ammoniated Pt clusters which are most mobile. Allowing sufficient time for the adsorbates to diffuse out of the pore structure before the temperature has risen to where cluster mobility begins allows the clusters to remain un-agglomerated. There is certainly a limiting ramp rate, below which no further benefit to cluster size is realized, and this is governed by the kinetics of diffusion of H_2O and NH_3 out of the zeolite. Conversely, growth of Pt clusters on non-microporous and more hydrophobic supports is often insensitive to the ramp rate, since the adsorbates are only weakly interactive with such materials.

The sinter-resistance of clusters in the present system during pyrolysis may be attributed to the "locking-in" of clusters within the (zeolite + polymer) matrix. This in itself is evidence for the ability of FFA to penetrate through the bulk of the microporous network, i.e., pore-blocking by Pt clusters is not frequent.

Current work is focused on optimizing cluster size control while increasing the fraction of Pt accessible to the fluid phase. A particular challenge to the preparation of model electrocatalysts is the generation of a carbon matrix with sufficient conductivity (requiring high-temperature pyrolysis) while maintaining a tight cluster size distribution.
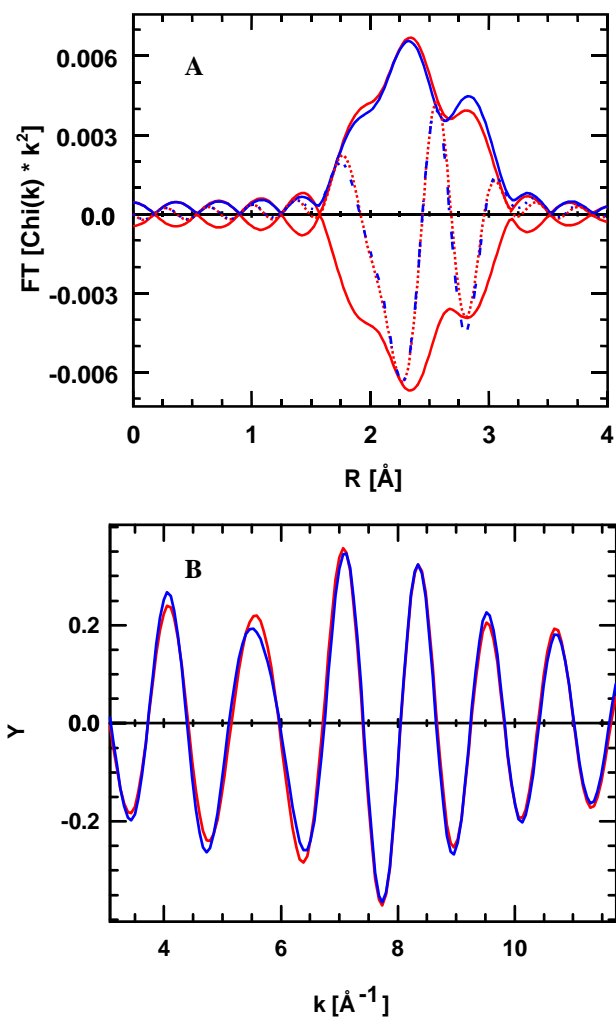
Acknowledgments

Figure 2. R-Space fit (A) and K-space fit (B) of isolated EXAFS data for [5]PtX(0.1:350) after reduction at 250°C under H_2. (k^2: $\Delta k = 3.05 – 11.70$ Å^{-1}, $\Delta r = 1.60 – 3.15$ Å). Red: data; Blue: fit; solid: real part; dotted: imaginary part.
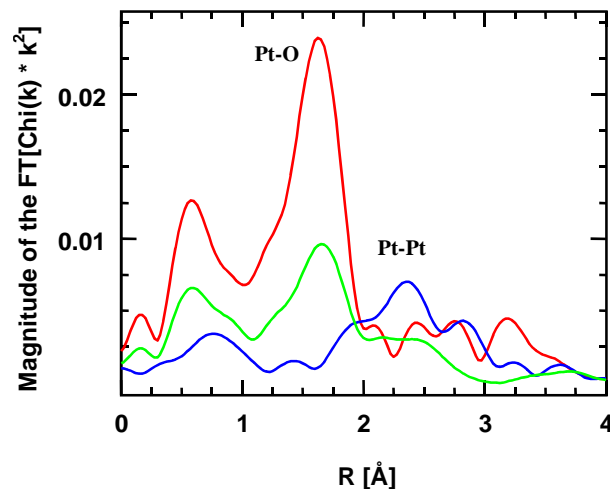

Figure 3. Magnitude of the Fourier Transform for [5]PtX(0.1:350) after various treatments: Red: calcined in air at 350°C; Blue: reduced under H_2 at 250°C; Green: exposed to ambient air after reduction (k^2: $\Delta k = 2.80 – 12.40$ Å^{-1})

References

1. Based on a state of the art electrocatalyst employing 0.5 g(Pt) kW^{-1}, a passenger vehicle would require ~25-50g Pt in its fuel cell; "Basic research needs for the hydrogen economy" Report of the Basic Energy Sciences Workshop on Hydrogen Production, Storage, and Use, May 13-15, 2003 [www.sc.doe.gov/bes/hydrogen.pdf].

2. (a) Boyen, H.-G.; Kästle, G.; Weigl, F.; Koslowski, B.; Dietrich, C.; Ziemann, P.; Spatz, J. P.; Riethmüller, S.; Hartmann, C.; Möller, M.; Schmid, G.; Garnier, M. G.; Oelhafen, P. *Science* **2002**, *297*, 1533-6. (b) Riley, S.J. In *Clusters of Atoms and Molecules II*, Haberland, H. Ed.; Springer Verlag: Berlin, (1994) p.226. (c) Riley, S.J.; Parks, *NATO ASI Ser. B*. **1987**, *158*, 727. (d) Cox, D. M.; Reichmann, K. C.; Trevor, D. J.; Kaldor, A. *J. Chem. Phys*. **1988**, *88(1)*, 111-9. (e) Pan, Y.H.; Sohlberg, K.; Ridge, D.P. *J. Am. Chem, Soc*. **1991**; *113*; 2406-2411. (f) Schnabel, P.; Irion, M.P.; Weil, K.G. *J. Phys. Chem*. **1991**, *95*, 9688-9694. (g) Xu, Z.; Xiao, F.-S; Purnell, S.K.; Alexeev, O.; Kawi, S.; Deutsch, S.E.; Gates, B.C. *Nature*, **1994**, *372*, 346-348.

3. Vaarkamp, M.; Miller, J.T.; Modica, F.S.; Lane, G.S.; Koningsberger, D.C. In P*roc. 10th Int. Congr. Catal*.; Guczi, L, et al., Eds.; Elsevier: Amsterdam, 1993, pp 809-820.

4. Kinoshita, K. *J. Electrochem. Soc*. **1990**, *137(3)*, 845-848.

5. (a) Homeyer, S. T.; Sachtler, W. M. H. *J. Cata*l., **1989**, *117(1)*, 91. (b) Homeyer, S. T.; Sachtler, W. M. H. *J. Catal*., **1989**, *118(1)*, 266. (c) Jacobs, P. A. *Stud. Surf. Sci. Catal*. **1986**, *29*, 357. (d) Gallezot, P. *Catal. Rev. Sci. Eng*. **1979**, *20*, 121.

6. a) de Graaf, J.; van Dillen, A. J.; de Jong, K. P.; Koningsberger, D. C. *J. Catal*. **2001**, *203*, 307-21. (b) Gallezot, P.; Alarcon-Diaz, A.; Dalmon, J.-A.; Renouprez, A.J.; Imelik, B. *J. Catal*., **1975**, *39*, 334-349. (c) Exner, D.; Jaeger, N.; Kleine, A.; Schulz-Ekloff, G. *J. Chem. Soc. Faraday Trans. I,* **1988**, *84(11)*, 4097-4104. (d) Rabo, J.A.; Schomaker, V.; Pickert, P.E. In *Proc. 3rd Int. Congr. Catal*.; Sachtler, W.M.H., Ed.; North-Holland: Amsterdam, 1965; Vol. 2, pp 1264-1276.

7. Serykh, A.I.; Tkachenko, O.P.; Borovkov, V.Yu.; Kazansky, V.B.; Beneke, M., Jaeger, N.I.; Schulz-Ekloff, G. *Phys. Chem. Chem. Phys*. **2000**, *2*, 5647-5652.

8. Coker, E. N.; Steen, W. A.; Abraham, I.C.; Miller, J. E. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*. **2004**, *49(2)*, 681-2.

9. (a) Coker, E. N.; Steen, W. A.; Kelly, M.J.; Miller, J. E. *J. Am. Chem. Soc*., submitted. (b) Coker, E. N.; Steen, W. A.; Widgeon, S.J.; Kelly, M.J.; Miller, J. T.; Kropf, A.J.; Miller, J. E., in preparation.