Effect of Pretreatment on Pt-Co/C Cathode Catalysts for the Oxygen-Reduction Reaction

***Elise B. Fox and Hector R. Colon-Mercado**

Savannah River National Laboratory, Aiken, SC 29808

*corresponding author: elise.fox@srnl.doe.gov, 8035078560

Carbon supported Pt and Pt-Co electrocatalysts for the oxygen reduction reaction in low temperature fuel cells were prepared by the reduction of the metal salts with sodium borohydride and sodium formate. The effect of surface treatment with nitric acid on the carbon surface and Co on the surface of carbon prior to the deposition of Pt was studied. The catalysts where Pt was deposited on treated carbon the ORR reaction preceded more through the two electron pathway and favored peroxide production, while the fresh carbon catalysts proceeded more through the four electron pathway to complete the oxygen reduction reaction. NaCOOH reduced Pt/C catalysts showed higher activity that $NaBH_4$ reduced Pt/C catalysts. It was determined that the Co addition has a higher impact on catalyst activity and active surface area when used with $NaBH_4$ as reducing agent as compared to NaCOOH.

Key words: oxygen reduction reaction, Co, Pt/C, rotating disk electrode, proton exchange membrane fuel cell

1. Introduction

Non-precious metal catalysts have been proposed for the replacement of platinum in low temperature fuel cells, however the low mass activity and low stability have prevented them from being successfully implemented [1-3]. The use of highly dispersed platinum crystallites on high surface area carbon can increase the active surface area and electrocatalytic activity of the catalysts, thereby reducing the Pt loadings in the cell. However, about four times the loading of the anode is currently used at the cathode to help compensate for the reaction kinetics due to the low activity of Pt electrocatalyst for the oxygen reduction reaction (ORR). Currently, Pt particles, with 2 to 3 nm in diameter, are loaded on high surface area carbon supports[4, 5]. Of the Pt loaded, only the surface atoms interact with the reactants. Although improvements in the catalytic activity by alloying Pt with transition metals has lead to lower loadings in the cathode, loadings are still one order of magnitude higher than the DOE target for 2015.

Co has been previously been studied in order to increase catalyst activity and stability for use in PEMFCs [6-10], however dissolution of the cobalt can occur and end up in other components of the fuel cell. During other investigations, a Co shell on Pt nanocrystals was produced where the thickness of the shell could easily be controlled by varying experimental parameters [11]. However, the process leaves Co in the outer shell, leaving it exposed to the corrosive cathode environment. Other reports have described the successful synthesis of Pt hollow spheres by colloidal dispersion methods with limited impurities remaining from the core metal [12]. However synthesis of the shell was often incomplete and in some cases continued growth of the Pt shell caused the structure to collapse and resulting nanoparticles had an irregular shape and reduced surface area. In order to increase the Pt utilization per metal particle, a non-noble transition metal, Co, was alloyed with a layer of Pt deposited on high surface area carbon. The transition metal was used as the seed for Pt crystallite growth in an effort to increase corrosion resistance of the particles. This approach previously demonstrated an enhancement of catalytic activity and stability of Pt/Pt alloys monolayers [13-15].

The present work investigates the effects of surface treatments and reducing agents on Pt-Co alloys to aid the future development of fuel cell catalysts with enhanced catalytic activity and stability using a "one pot" simple method. Synthesized catalysts were characterized for electrochemical activity by RRDE and their morphology studied with transmission electron microscopy.

2. Experimental

2.1 Catalyst Synthesis

To treat the carbon, a solution of 70 wt.% HNO_3 was mixed with the carbon support (Ketjen Black EC-600JD, AkzoNobel Corporate) in a ratio of 4 g of carbon support for every 200 mL of acid solution, heated to 80°C and refluxed for seven hours. The solution was then allowed to cool and the solids allowed to settle. The solution was decanted and the carbon was washed with DI-water. Once the carbon support was filtered and washed with DI-water, the material was allowed to dry overnight in a vacuum oven at 80 ºC. This introduces oxygen containing groups to the carbon support via quinone-hydroquinone redox couple [16-18].

To make Co-C, the activated carbon previously prepared was mixed with a transition metal salt such as cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$) in water (8.7 g of cobalt salt in 220 mL of DI-water). The pH of the solution was reduced to three by the addition of nitric acid. The dispersion was heated to 90 ºC using a water bath. After a stable temperature was attained, 5.4 g of urea dissolved in 60 mL of DI-water was added. After 16 hours and when the dispersion pH was close to neutral, the suspension was cooled , filtered, washed with DI-water and dried at 120 ºC in an oven [19].

The desired amount of the precious metal salt (H_2PtCl_6) to achieve a Pt loading of 15 wt% was mixed with the either the carbon support or Co-C suspended in water (600 mL). The solution was then ultrasonically mixed and placed inside the cylindrical reaction flask. The reducing agent (NaCOOH [4, 20] or $NaBH_4$) was added dropwise to the solution in the heated reaction flask (90 ºC) either before or after the Pt salt in order to help determine its effects on activity. The reducing agent in solution was added in excess to account for deactivation during the dropwise addition After all the reducing agent was added, the suspension was stirred at the temperature for 20 hours to allow the colloidal Pt particles to adsorb on the support surface. The suspension was filtered with a membrane filter Buchner funnel set-up and washed with deionized water. The recovered solid was then vacuum-dried at 80 ºC for two hours.

2.2 Catalyst Characterization

A Pine Instruments Rotating Ring Disk Electrode (RRDE) provided data on the kinetics of the reaction at the cathode. An ink of approximately 9 mg of catalyst in 4 mL of DI H_2O was made. 30 μL was deposited on the glassy carbon (5 mm diameter disc) surface and allowed to dry. The catalyst was then coated with 8 μL of a 20% Nafion/ethanol solution. The RDE current output during the potential sweep was used to determine the electrode reactions in 0.5M H_2SO_4 [21, 22]. A Pt foil counter electrode and

Ag/AgCl reference electrode were used. Cyclic voltagrams were collected under a N_2 blanket at 50 mV/s. The solution was then saturated with O_2 and linear sweep measurements were recorded from 100-1200 rpm at 5 mV/s. All potentials were normalized to the standard hydrogen electrode (SHE). During the linear sweeps the Pt ring potential was maintained at 1.2V versus SHE to oxidize any peroxide produced. The number of electrons transferred (*n*) can be determined by the following equation [17]:

$$n = \frac{4I_D}{I_D + \frac{I_R}{N}}$$

where N, I_D and I_R are the collection efficiency, disk current and ring current, respectively. We assumed the collection efficiency to be constant at a theoretical value of 0.256 for all the catalysts studied. All measurements were taken using a bipotentiostat (Model AFCBP1 from Pine Instruments).

Samples were prepared for TEM analysis by grinding with a mortar and pestle and preparing a suspension of the catalyst in ethanol, which was applied to a carbon grid. Samples were analyzed on a JEOL JEM 2010 analytical transmission electron microscope.

ICP-MS was completed on catalysts samples to determine composition. The catalysts were dissolved using the aqua regia method and analyzed on a Plasma Quad II.

3.0 Results and Discussion

TEM was used to determine the particle size and surface morphology of the catalyst. The TEM of the Pt/C catalysts is shown in Figure 1, where the darker areas indicate Pt particles and gray areas indicate carbon support. The Pt particles sizes were independent of the reducing agent with all catalyst Pt particle sizes at about 3 nm, while the dispersion of Pt on the carbon surface depends mostly on the pre-treatment of the support. Pt particles deposited on treated carbon, tend to form conglomerates. This effect is magnified on the catalysts prepared using $NaBH_4$ as reducing agent.

Figure 2 shows the polarization curves of the Pt/C catalysts obtained at room temperature and in 0.5M H_2SO_4 saturated with O_2 using a RDE at 800 rpm. The insert shows the number of electrons towards the ORR calculated from the ring currents. At high potentials, the ORR is under the kinetic-diffusion control region. This region is followed by a purely diffusion limited region starting in most cases between 0.55 and 0.35 V versus SHE [23]. The kinetic-diffusion control region was compared between the different catalysts to study the effect of reducing agent and carbon support treatment. The potential at the midpoint of the difference of the limiting and the residual current or the half wave potential for each catalyst is reported in Table 1. The highest half wave potential was obtained for the Pt catalyst prepared with fresh carbon support combined with the sodium formate reducing agent (0.767 V) followed by the $NaBH_4$ reduced catalysts on fresh carbon support (0.711 V). The performance was the same for the Pt catalysts reduced on treated carbon when either reducing agent is used (0.629 V). Commercial 20 wt % Pt on Vulcan-XC from BASF was used as a comparison (0.794V). The selectivity towards the four electron transfer for the ORR was measured by the ring currents. Values closer to two electrons indicate the incomplete reduction of oxygen to water and instead yielding peroxide. The ring data is shown at potentials between 0.4 and 0.75 V vs. SHE in order to prevent the interference of the hydrogen adsorption-desorption peak and the error from the negligible ring currents, respectively [24, 25]. Overall, the catalysts where Pt was deposited on treated carbon shows a lower number of electrons, while the catalysts prepared with fresh carbon shows higher number of electrons towards complete ORR.

Figure 3 shows the CVs obtained for commercial 20 wt% Pt/C and reduced Pt/C catalysts with $NaBH_4$ and NaCOOH on untreated and treated carbon support. Two major peaks can be identified from the CV. At potentials higher than 0.65 V the oxidation–reduction of Pt is observed. At potentials below 0.2 V, the desorption–adsorption of hydrogen on the Pt surface is observed [24]. The area under the hydrogen desorption peak was used to calculate the electrochemical surface area. A conventional electrochemical method based on the electrical charge required for the hydrogen adsorption–desorption on a polycrystalline Pt surface area (210 μCcm^{-2}) was used [26]. Table 1 summarizes the electrochemical surface area from the hydrogen desorption peak integration. The highest surface area is observed for the commercial catalyst followed by the NaCOOH and then the $NaBH_4$ reduced catalyst on untreated carbon support. In the case of catalysts prepared on treated support an additional peak is observed at around 0.55V (SHE). This peak is characteristic of the surface oxide groups redox couples [10, 27] formed during the surface treatment with nitric acid. Surface treatments incorporate oxygen surface groups that help increase the metal dispersion on the support, however some oxygen surface groups may not be stable during the catalysts preparation and their decomposition favors agglomeration and sintering of the metal particles [28]. This is the case of the prepared catalysts on treated carbon where the surface area decreased due to particle agglomeration as seen on the TEM micrograph. This may also account for the decrease in the kinetic activity as seen in Figure 2.

In attempt to further improve the activity of the Pt/C catalysts, cobalt was added to the base carbon support. Co was first deposited on the carbon support followed by Pt. Co is expected to serve as a nucleation site for Pt precipitation and therefore increase the activity of by Pt-Co interaction and increasing the active surface area of the metal sites. Figure 4 and Figure 5 show the effects of Co deposited on fresh, untreated carbon on the ORR activity and active surface area, respectively. Note that the reducing agent was added after the platinum metal salt was added. When $NaBH_4$ is used as a reducing agent in untreated carbon, cobalt has a positive effect in both the activity for the ORR and the electrochemical active surface area. In the case of the catalyst reduced with NaCOOH the effect of the Co is detrimental as compared to the catalyst prepared without Co. When $NaBH_4$ is used as the reducing agent, the active surface area increases when Co is added to Pt/C catalyst, but the active surface area decreases for Pt-Co/C when NaCOOH is used. The half wave potential for the prepared catalysts is highest for the Pt-Co/C catalyst prepared with the sodium borohydride reducing agent (0.742 V) followed by the sodium formate reduced catalysts on fresh carbon support (0.735 V). This result suggests that cobalt is more beneficial when a strong reducing agent is used for the reduction of cobalt and platinum species. When a weak reducing agent is used, such as sodium formate, the incomplete reduction of cobalt on the carbon surface prevents the platinum from occupying the nucleation sites, while using a strong reducing agent allows the cobalt to get reduced and be nucleation sites for the platinum nanoparticles.

In order to determine if the order of the reducing agent addition to the solution effected Pt deposition on Co/C tests were carried out on treated carbon supports using $NaBH_4$ as the reducing agent. Figure 6 and Figure 7 show the effects of reducing agent addition order on the ORR activity and active surface area, respectively. The addition of reducing agent before the Pt salt is thought to help by reducing the cobalt nanoparticles before the Pt salt is added. Consequently, the reduced cobalt will then reduce the Pt salt by galvanic displacement [12]. Unfortunately, the desired effects were not observed in the results. The lower active surface area and ORR activity can be attributed to the consumption/decomposition of the reducing agent by Co reduction and therefore a lack of reducing power to reduce the Pt salt on the support surface. When the reducing agent is added after the Pt salt, the corresponding ORR activity and surface area of the catalysts on the treated support increases to values close to those when the untreated support is used. The half wave potential was higher for the catalyst prepared with the reducing agent added after (second) to the platinum salt (0.770 V) followed by the reducing agent added before (first) the Pt salt (0.610 V).

4.0 Conclusions

The effect of carbon surface oxidation and cobalt nanoparticles incorporation on the activity of Pt/C catalysts was studied. The Pt/C samples reduced with sodium formate did not benefit from carbon support oxidation or Co incorporation. However, NaCOOH reduced Pt/C catalysts have a higher activity that $NaBH_4$ Pt/C catalysts. When sodium borohydride is used as the reducing agent on treated carbon, the addition of Co helped increase the dispersion of the Pt and the surface area approaches that of fresh carbon. The best performance towards the ORR was observed when sodium borohydride is used to reduce Pt on Co incorporated treated carbon followed by when sodium formate is used to reduce Pt on Co incorporated fresh carbon . It was determined that the Co addition has a higher impact on catalyst when used with $NaBH_4$ as reducing agent as compared to NaCOOH.

The combination of linear sweep and cyclic voltammetry can help explain the effects of the different preparation procedures used on the ORR. Typically the more reaction sites on a catalyst surface the better the ORR currents. In turn, the lower the ring currents, the lower the production of peroxide. When low surface area is measured, the ring currents increase and more peroxide is produced. This can be seen as an indication of more of the carbon surface taking part on the oxygen reduction reaction, as treated carbon usually promotes the formation of peroxide [29]. This is exemplified by the comparison of Pt/C using treated and untreated supports. When the treated support is used, the reaction proceeds closer to the two electron pathway versus the four electron pathway. The treated supports also had great conglomeration of Pt particles and therefore greater carbon surface area available for the reaction.

Acknowledgment

This work was funded under SRNL FY08 LDRD Programs and SRNL Mini-Sabbatical. Savannah River National Laboratory is operated by Savannah River Nuclear Solutions. This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

References

[1] R.T. Atanasoki, Novel Approach to Non-Precious Metal Catalysts , 2007 DOE Hydrogen Program Review: Washington, DC.

[2] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs, Appl. Catal. B: Environ. 56 (2005) 9-35.

[3] B. Li, J. Qiao, J. Zheng, D. Yang, J. Ma, Carbon-supported Ir-V nanoparticle as novel platinum-free anodic catalysts in proton exchange membrane fuel cell, Int. J. Hydro. Energy 34 (2009) 5144-5151.
[4] F.J. Nores-Pondal, I.M.J. Vilella, H. Troiani, M. Granada, S.R. de Miguel, O.A. Scelza, H.R. Corti, Catalytic activity vs. size correlation in platinum catalysts of PEM fuel cells prepared on carbon black by different methods, Int. J. Hydro. Energy 34 (2009) 8193-8203.
[5] E.P. Ambrosio, C. Franca, M. Manzoli, N. Penazzi, P. Spinelli, Platinum catalyst supported on mesoporous carbon for PEMFC, Int. J. Hydro. Energy 33 (2008) 3142-3145.
[6] X. Li, H.R. Colón-Mercado, G. Wu, J.-W. Lee, B.N. Popov, Development of method for synthesis of Pt-Co cathode catalysts for PEM fuel cells, Electrochem. Solid-State Lett. 10 (2007) B201-B205.
[7] A.K. Shukla, M. Neergat, P. Bera, V. Jayaram, M.S. Hegde, An XPS study on binary and ternary alloys of transition metals with platinized carbon and its bearing upon oxygen electroreduction in direct methanol fuel cells, J. Electroanal. Chem. 504 (2001) 111-119.
[8] A.S. Arico, A.K. Shukla, H. Kim, S. Park, M. Min, V. Antonucci, An XPS study on oxidation states of Pt and its alloys with Co and Cr and its relevance to electroreduction of oxygen, Appl. Surf. Sci. 172 (2001) 33-40.
[9] H.R. Colón-Mercado, B.N. Popov, Stability of platinum based alloy cathode catalysts in PEM fuel cells, J. Power Sources 155 (2006) 253-263.
[10] N.P. Subramanian, S.P. Kumaraguru, H.R. Colon-Mercado, H. Kim, B.N. Popov, T. Black, D.A. Chen, Studies on Co-based catalysts supported on modified carbon substrates for PEMFC cathodes, J. Power Sources 157 (2006) 56-63.
[11] N.S. Sobal, U. Ebels, H. Mohwald, M. Giersig, Synthesis of Core-Shell PtCo Nanocrystals, J. Phys. Chem. B 107 (2003) 7351-7354.
[12] J. Li, Y. Liang, Q.-C. Xu, X.-Z. Fu, J.Q. Xu, J.-D. Lin, D.-W. Liao, Synthesis and characterization of sub-10 nm platinum hollow spheres as electrocatalyst of direct methanol fuel cell, J. Nanosci. Nanotech. 6 (2006) 1107-1113.
[13] M.B. Vukmirovic, J. Zhang, K. Sasaki, A.U. Nilekar, F. Uribe, M. Mavrikakis, R.R. Adzic, Platinum monolayer electrocatalysts for oxygen reduction, Electrochem. Acta 52 (2007) 2257-2263.
[14] Y. Yin, R.M. Rioux, C. Erdonmez, S. Hughes, G.A. Somorjai, A.P. Alivisatos, Formation of nanocrystals through the nanoscale Kirkendall effect, Science 304 (2004) 711-714.
[15] S. Guo, Y. Fang, S. Dong, E. Wang, High-efficency and low-cost hybrid nanomaterial as enhancing electrocatalyst: spongelike Au/Pt core/shell nanomaterial with hollow cavity, J. Phys. Chem. C 111 (2007) 17104-17109.
[16] W. H., R. Ct, G. Faubert, D. Guay, J.P. Dodelet, Effect of pre-treatment on of the carbon black supports on the activity of Fe-based electrocatalysts for the reduction of oxygen, J. Phys. Chem. B 103 (1999) 2042-2049.
[17] N.P. Subramanian, S.P. Kumaraguru, H. Colon-Mercado, H. Kim, B.N. Popov, T. Black, D.A. Chen, Studies on Co-based catalysts supported on modified carbon substrates for PEMFC cathodes, J. Power Sources 157 (2006) 56-63.
[18] S.C. Ball, S.L. Hudson, D. Thompsett, B. Theobald, An investigation into factors affecting the stability of carbons and carbon supported platinum and platinum/cobalt

alloy catalysts during 1.2 V potentiostatic hold regimes at a range of temperatures, J. Power Sources 171 (2007) 18-25.
[19] J.H. Bitter, M.K. van der Lee, A.G.T. Slotboom, A.J. van Dillen, K.P. de Jong, Synthesis of highly loaded highly dispersed nickel on carbon nanofibers by homogeneous deposition-precipitation, Catal. Let. 89 (2003) 139-142.
[20] L. Xiong, A. Manthiram, Synthesis and characterization of methanol tolerant Pt/TiOx/C nanocomposites for oxygen reduction in direct methanol fuel Cells, Electrochimica Acta 49 (2004) 4163-4170.
[21] J.N. Soderberg, A.H.C. Sirk, S.A. Campbell, V.I. Birss, Oxygen reduction by sol-gel derived Pt/Co- based alloys for PEM fuel cells, J. Electrochem. Soc. 152 (2005) A2017-A2022.
[22] H.A. Gasteiger, N.M. Markovic, P.N. Ross Jr., H_2 and CO electrooxidation on well-characterized Pt, Ru, and Pt-Ru 2. Rotating disk electrode studies of CO/H_2 mixtures at 62°C, J. Phys. Chem. 99 (1995) 16757-16767.
[23] A.J. Bard, L.R. Faulkner, Electrochemical Methods, in: Editor, (Eds.), John Wiley & Sons: New York. 2001.
[24] U.A. Paulus, A. Wokam, G.G. Scherer, T.J. Schmidt, V. Stamenkovic, N.M. Markovic, P.N. Ross, Oxygen reduction on high surface area Pt-based alloy catalysts in comparison to well defined smooth bulk alloy electrodes, Electrochimica Acta 47 (2002) 3787-3798.
[25] S. Murkerjee, S. Srinivasan, M.P. Soriaga, J. McBreen, Effect of preparation conditions of Pt alloys on their electronic, structural, and electrocatalytic activites for oxygen reduction- XRD, XAS, and electrochemical studies, J. Phys. Chem. 99 (1995) 4577-4589.
[26] T. Toda, H. Igarashi, M. Watanabe, Enhancement of the electrocatalytic O_2 reduction on Pt-Fe alloys, J. Electroanal. Chem. 460 (1999) 258-260.
[27] L. Li, Y. Xing, J. Electrochem. Soc. 153 (2006) A1823-A1828.
[28] X. Yu, S. Ye, Recent advances in activity and durability enhancement of Pt/C catalytic cathode in PEMFC Part I. Physico-chemical and electronic interaction between Pt and carbon support, and activity enhancement of Pt/C catalyst, J. Power Sources 172 (2007) 133-144.
[29] N.P. Subramanian, X. Li, V. Nallathambi, S.P. Kumaraguru, H. Colon-Mercado, G. Wu, J.-W. Lee, B.N. Popov, Nitrogen-modified carbon-based cataysts for oxygen reduction reaction in polymer electrolyte fuel cells, J. Powers Sources 188 (2009) 38-44.

Figure 1: TEM of Pt/C catalysts, scale is 25 nm. (A) $NaBH_4$ on treated carbon (B) $NaBH_4$ on fresh carbon (C) NaCOOH on treated carbon (D) NaCOOH on fresh carbon

Figure 2: Effect of carbon support treatment on the ORR activity of Pt/C catalysts at 800 rpm: (1) fresh carbon with $NaBH_4$ (2) treated carbon with NaCOOH (3) treated carbon with $NaBH_4$ (4) fresh carbon with NaCOOH (5) BASF 20%Pt/C

Figure 3: Effect of carbon support treatment on the cyclic voltammetry of Pt/C : (1) fresh carbon with $NaBH_4$ (2) treated carbon with NaCOOH (3) treated carbon with $NaBH_4$ (4) fresh carbon with NaCOOH (5) BASF 20%Pt/C.

Figure 4: Effect of the reducing agent on the ORR activity of Pt-Co/C using untreated carbon support at 800 rpm in O_2 saturated H_2SO_4. (1) NaCOOH reducing agent (2) $NaBH_4$ reducing agent

Figure 5: Effect of the reducing agent on the cyclic voltammogram of Pt-Co/C using untreated carbon support. (1) NaCOOH reducing agent (2) $NaBH_4$ reducing agent

Figure 6: Effect of the addition of the reducing agent order ($NaBH_4$) on the ORR activity of Pt-Co/C using treated carbon support at 800 rpm. (1) reducing agent added before the Pt salt (2) reducing agent added after Pt salt

Figure 7: Effect of the addition of the reducing agent order ($NaBH_4$) on the cyclic voltammogram of Pt-Co/C using treated carbon support. (1) reducing agent added before the Pt salt (2) reducing agent added after Pt salt