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

E. B. Fox
H. R. Colón-Mercado

May 2009
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E. B. Fox
H. R. Colón-Mercado

May 2009
# REVIEWS AND APPROVALS

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EXECUTIVE SUMMARY

In order to reduce the precious metal loading without sacrificing activity and stability, a new method for the preparation of bimetallic catalysts is proposed. Currently, Pt-alloy particles, with 2 to 3 nm in diameter, are loaded on high surface area carbon supports. Of the Pt loaded, only the surface atoms interact with the reactants. In order to increase the Pt utilization per metal particle the new process for catalyst preparation will incorporate a non-noble transition metal core coated with a skin layer of Pt deposited on high surface area carbon. The effect of reducing agent strength during synthesis was also explored. It was determined that the Co addition has a higher impact on catalyst when used with NaBH₄ as reducing agent as compared to NaCOOH.
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LIST OF ABBREVIATIONS

HOR  Hydrogen Oxidation Reaction
ICP-MS  Inductively Coupled Plasma- Mass Spectrometry
ORR  Oxygen Reduction Reaction
TEM  Transmission Electron Microscopy
1.0 Introduction

The use of highly dispersed platinum crystallites on high surface area carbon increases the active surface area and electrocatalytic activity of the electrocatalysts, thereby reducing the Pt loadings in the cell. About four times the loading of the anode is currently used at the cathode to help account for the low activity of the Pt electrocatalyst for the oxygen reduction reaction (ORR). 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]. Although improvement in 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. In order to reduce the precious metal loading without sacrificing activity and stability, a new method for the preparation of bimetallic catalysts is proposed. Currently, Pt-alloy particles, with 2 to 3 nm in diameter, are loaded on high surface area carbon supports. Of the Pt loaded, only the surface atoms interact with the reactants. In order to increase the Pt utilization per metal particle the new process for catalyst preparation will incorporate a non-noble transition metal core coated with a skin layer of Pt deposited on high surface area carbon. This approach was proved by Mukmirovic et al [2], demonstrating an enhancement of catalytic activity and stability of Pt/Pt alloys monolayers by galvanic displacement of a copper monolayer on a palladium single crystal and on palladium particles supported on carbon. However the use of palladium as the metal core still has the disadvantage of high price. The objective of this work is to develop a cost effective method that will improve the utilization of Pt while increasing the catalysts activity and durability through alloy formation.

During investigation of a Co shell on Pt nanocrystals, it was found that the thickness of the shell can easily be controlled by varying experimental parameters [3]. However, care must be taken to ensure that complete coverage of the core nanocrystals is complete, while limiting the generation of individual metal crystals which can serve as islands during crystallization. Other
reports have described the successful synthesis of Pt hollow spheres by colloidal dispersion methods with limited impurities remaining from the core metal [4]. 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.

In order to drive down the cost of fuel cells, while keeping the activity and stability of the catalyst high, the preparation of a transition metal cores coated with platinum and platinum alloy monolayer was attempted. Synthesized catalysts were characterized for electrochemical activity.

2.0 Experimental Procedure

To treat the carbon, a solution of 70 wt.% HNO₃ was mixed with the carbon support 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 is then allowed to cool and the solids are allowed to settle. The solution is decanted and the carbon is washed with DI-water. Once the carbon support has being filtered and washed with DI-water, the material is allowed to dry overnight in a vacuum oven at 80 ºC.

To make Co-C, the activated carbon previously prepared is then mixed with a transition metal salt such as cobalt nitrate (Co(NO₃)₂·6H₂O) in water (8.7 g of cobalt salt in 220 mL of DI-water). The pH of the solution is adjusted to three by adding nitric acid. The temperature of the dispersion is increased to 90 ºC by using a water bath. After a stable temperature is attained 5.4 g of urea dissolved in 60 mL of DI-water are added. After 16 hours and when the dispersion pH is close to neutral, the suspension is cooled, filtered, washed with DI-water and dried at 120 ºC in an oven [5].

The desired amounts of the precious metal salt (H₂PtCl₆) was mixed with the either the carbon support or Co-C suspended on water (600 mL). The solution was then ultrasonically mixed and placed inside the cylindrical reaction flask. The reducing agent (NaCOOH [6] or NaBH₄) was added at 10X excess when the solution in the reaction flask reached the reaction
temperature of 90 °C. 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 the membrane filter set-up and washed with deionized water. The recovered solid was then vacuum-dried at 80 °C for two hours. The reducing agent was added to the solution either before or after the Pt salt in order to help determine its effects on activity.

A Pine Instruments Rotating disk electrode (RDE) provided data on the kinetics of the reaction at the cathode. An ink if approximately 9 mg of catalyst in 4 mL of DI H₂O was made. 30 µL was deposited on the glassy carbon surface and allowed to dry. The catalyst was then coated with 8 µL of a 20% Nafion/ethanol solution. The RRDE outputs a current-voltage reading during the catalyst reaction with 0.5M H₂SO₄, which can be used to determine the potential for ORR [7, 8]. A Pt foil counter electrode and Ag/AgCl reference electrode were used. Cyclic voltamgrams were collected under a N₂ blanket. The solution was then saturated with O₂ and linear sweep measurements were recorded from 100-1200 rpm. All potentials are normalized to the standard hydrogen electrode (SHE).

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

Figure 1 shows a typical polarization curve of the Pt/C catalysts obtained at room temperature and in 0.3M H₂SO₄ saturated with O₂ using a GCRDE at 800 rpm. 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 RHE. The kinetic-diffusion control region was compared between the different catalysts to study the effect
of reducing agent and carbon support treatment. At a current of -2 mA/g$_{\text{catalyst}}$ the highest voltage is obtained for the catalyst prepared with fresh carbon support combined with the sodium formate reducing agent (0.79 V) followed by the NaBH$_4$ reduced catalysts (0.73 V) which had the same performance regardless of carbon support treatment. The treated carbon with the NaCOOH reduction performed similarly to both NaBH$_4$ reduced catalysts (0.72 V). These results indicate for pure Pt deposition on carbon black, the fresh carbon gives higher activity.

ICP-MS and TEM was used to determine the amount of Pt deposited and the particle size and surface morphology of the support. The Pt loading of the catalysts is reported in Table 1. While the target loading of the catalysts was 20% Pt, all four catalysts had lower amounts of deposited metal in the samples. NaBH$_4$ reduced samples had identical loadings of 13.9%. The NaCOOH catalyst on fresh carbon had the highest metal loading of 15.4%. This increase in metal accounts for part of the increase in catalyst activity.
Figure 1: Effect of carbon support treatment on activity of Pt/C catalysts at 800 rpm. (1) fresh carbon with NaBH₄ (2) treated carbon with NaCOOH (3) treated carbon with NaBH₄ (4) fresh carbon with NaCOOH (5) BASF 20%Pt/C.
Table 1: Catalyst composition and electrochemical surface area as determined by ICP-MS and cyclic voltammograms, respectively.

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<th>Electrochemical Surface Area- m²/gPt</th>
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<tr>
<td>NaBH₄ on untreated carbon</td>
<td>13.9%</td>
<td>2.70</td>
</tr>
<tr>
<td>NaBH₄ on treated carbon</td>
<td>13.9%</td>
<td>----</td>
</tr>
<tr>
<td>NaCOOH on untreated carbon</td>
<td>15.4%</td>
<td>11.42</td>
</tr>
<tr>
<td>NaCOOH on treated carbon</td>
<td>12.6%</td>
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<td>BASF commercial</td>
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<td>22.55</td>
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The TEM of the Pt/C catalysts is shown in Figure 2, where the darker areas indicate Pt particles and gray areas indicate carbon support. While the average particle size depends on the reducing agent, the dispersion on the carbon surface depends on the pre-treatment of the support. Samples reduced with NaBH₄ have an average particle size of 3.6 nm while samples reduced with NaCOOH have an average particle size of 2.4 nm. Pt particles deposited on treated carbon tend to form conglomerates. This effect is magnified on the catalysts prepared using NaBH₄ as reducing agent.
Figure 2: TEM of Pt/C catalysts, scale is 100nm. (A) NaBH₄ on treated carbon (B) NaBH₄ on fresh carbon (C) NaCOOH on treated carbon (D) NaCOOH on fresh carbon

Figure 3 shows a typical CV obtained for commercial 20 wt% Pt/C and reduced catalysts with NaBH₄ and NaCOOH on untreated carbon support. The 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. 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 [9]. The highest hydrogen desorption-adsorption peak is observed for the commercial catalyst followed by the NaCOOH reduced and then the NaBH$_4$ reduced catalyst. The reduction in peak area can be attributed to the increase in particle size as observed by the TEM micrographs. The larger the peak area, the higher the electrochemical surface area of the catalyst available for reaction (see Table 1).

![Figure 3: Effect of reducing agent on Pt/C catalyst activity on an untreated carbon support. (1) BASF 20%Pt/C (2) NaCOOH (3) NaBH$_4$](image)

In attempts to improve the activity of the Pt/C catalysts, 30 wt% Co was added to the base support. Co was first deposited on the carbon support followed by Pt. It is believed that the Co will serve as a nucleation site for Pt precipitation and create a particle with a Co metal core
and Pt outer shell. This will help increase the activity of the Pt metal both through alloying effects and by increasing the active surface area of the metal sites. Figure 4 and Figure 5 show the effect of Co on the catalyst active surface area and ORR activity, respectively, when using NaCOOH as a reducing agent in untreated carbon. As can be seen in Figure 4 the addition of the cobalt reduces slightly the active surface area of the platinum. Although a small reduction in surface area, the effect on the activity is more visible (see Figure 5). At -2 mA/g_catalyst the potential decreases when cobalt is incorporated on the support from 0.79 V to 0.77 V. While the mass transport current is higher for the sample with the cobalt, the mass transport current is not as defined as in the Pt/C electrode.

Figure 4: Effect of Co addition on the cyclic voltammogram of Pt/C using untreated carbon support with NaCOOH reducing agent. (1) Pt-Co/C (2) Pt/C
Figure 5: Effect of Co addition on the polarization curve of Pt/C using the untreated carbon support with NaCOOH reducing agent.

The Co addition has a much larger effect on catalyst activity when NaBH$_4$ is used as the reducing agent. Figure 6 and Figure 7 shows the effect of Co on the catalyst active surface area and ORR activity, respectively, when using NaBH$_4$ as a reducing agent in untreated carbon. As can be seen in Figure 6 the addition of the cobalt increases the active surface area of the platinum. The activity for the ORR is similar for both samples. At -2 mA/g$_\text{catalyst}$ the potential when cobalt is incorporated on the support is 0.728 V while 0.735 V vs. SHE for the Pt on the untreated carbon support. As seen in the previous plot, the mass transport limited current is less defined but higher for the catalyst with cobalt in the support.
Figure 6: Effect of Co addition on activity of Pt/C using the untreated carbon support with NaBH₄ reducing agent. (1) Pt-Co/C (2) Pt/C
Figure 7: Effect of Co addition on activity of Pt/C using the untreated carbon support with NaBH$_4$ reducing agent at 800 rpm.

To further investigate the effect of the addition of cobalt on the support, the catalyst performance was evaluated on catalysts prepared with treated carbon support and reduced with NaBH$_4$. The order at which the addition of NaBH$_4$ was added was changed from after the addition of Pt salt to the solution to after. Figure 8 shows the effect of the preparation on the cyclic voltammogram. With the oxidation step of the carbon support a well-defined redox peaks at about 0.55V (SHE) is formed. This peak is characteristic of the quinine-hydroquinone redox couple [10]. A similar peak is also observed in samples where cobalt was incorporated, where the nitrate from the cobalt salt oxidizes the carbon support. From the plot can also be observed the hydrogen adsorption-desorption peak is almost absent in the samples where no cobalt is used or in the sample where the reducing agent is added before the addition of the Pt solution. Figure 9 shows the effect on the
activity for the ORR. When the NaBH$_4$ is added and stirred for 10 minutes prior to the Pt salt addition, at a current of -2 mA/g$\text{catalyst}$ the operating voltage of 0.67 V. When the reducing agent is added 10 minutes after the salt solution, the corresponding voltage was measured 0.80 V. The Pt deposited on treated carbon and reduced with NaBH$_4$ in the absence of Co was included in the figure for comparison.

Figure 8: Effect of order of NaBH$_4$ addition on Pt-Co/C catalyst activity using treated carbon. (1) addition to solution before Pt salt (2) Pt deposited on treated carbon with NaBH$_4$ (3) addition to solution after Pt salt.
Figure 9: Effect of order of NaBH₄ addition on Pt-Co/C catalyst activity at 800rpm, using treated carbon. (1) addition to solution before Pt salt (2) Pt deposited on treated carbon with NaBH₄ (3) addition to solution after Pt salt.

Table 2 summarizes the electrochemical surface areas of the different prepared samples. In general the samples reduced with sodium formate don’t benefit from the oxidation or Co incorporation in the carbon support. On the other hand when sodium borohydride is used as the reducing agent on treated carbon, the addition of Co help increase the dispersion of the Pt and the surface area approaches that of un-treated carbon.

The effect of Co on the mass transport limited region is observed in all the figures, where the incorporation of Co increases the mass transport limited current. It is speculated that during the catalysts preparation, the Co nanoparticles aid in the deposition
of the Pt to the surface of the carbon support and prevents the Pt salt from depositing into the pores of the carbon, therefore enhancing the access of the Pt to dissolved oxygen. This result can be confirmed with BET surface area analysis which shows the addition of cobalt enhances the surface area of the catalyst (32.7 m²/g for the Pt deposited on treated carbon and NaBH₄ as reducing agent vs. 171.6 m²/g for Pt deposited on treated Co-carbon and NaBH₄ as reducing agent added second).

Table 2: Catalyst electrochemical surface area as determined cyclic voltammograms

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<th>Electrochemical Surface Area- m²/g&lt;sub&gt;catalyst&lt;/sub&gt;</th>
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<tr>
<td>Pt deposited on untreated carbon (NaCOOH)</td>
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<td>Pt deposited on untreated Co-carbon (NaCOOH)</td>
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<td>Pt deposited on untreated carbon (NaBH₄)</td>
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4.0 Conclusions

The effect of carbon surface oxidation and cobalt nanoparticles incorporation was studied.

The best performance is observed when sodium formate is used to reduce Pt on the fresh carbon surface. The effect of cobalt in all cases where NaBH$_4$ is used enhances the activity and surface area of the catalysts. Cobalt addition seems to enhance the mass transport limited current.

5.0 References

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