An Efficient Electrocatalyst (PtCo/C) for the Oxygen Reduction Reaction

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Abstract: The oxygen reduction reaction (ORR) is paid much more attention because of the high overpotential required for driving the four-electron process in the field of storage and sustainable energy conversion, including fuel cell applications. In this paper, PtCo nanoparticles encapsulated on carbon supports were prepared by a simple modified polyol method with ethylene glycol. Structural as well as electrochemical characterizations illustrated that the PtCo/C electrocatalysts had a minimum particle size of 4.8 nm, which is close to the commercial 40 wt% Pt/JM. Moreover, the electrochemical measurements indicated that ORR activity was competitive with the commercial 40 wt% Pt/JM catalyst. The synthesis method is a critical way to produce PtCo/C catalysts for use in polymer electrolyte membranes in fuel cells (PEMFCs).

Keywords: proton exchange membrane fuel cells; oxygen reduction reaction; PtCo nanoparticles; modified polyol method

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are typical substances that produce electricity from chemical energy [1–3]. Among the components of PEMFCs, the most practical electro catalysts are carbon-supported Pt catalysts, due to their having the highest activity in the oxygen reduction reaction (ORR) [4–13]. However, real-life applications of Pt/C are few due to their high cost and low availability, as well as their poor stability [14,15].

Recently, many efforts have been taken to develop low-platinum-based ORR catalysts such as PtCo/C catalysts and so on. PtCo/C catalysts have been studied a lot for the ORR. For instance, Loukrakpam et al. [16] studied PtCo/C catalysts using oleic and oleylamine acids, and came to the conclusion that the electrocatalytic activity increased with decreases in the nanoparticle size of the PtCo alloy. The Pt 75Co 25/C catalyst particle size was 2.8 nm, with an ORR mass activity of 270 mA mgPt −1—which was the highest observed. Jayasayee et al. [17] found that at 950 °C, Pt 75Co 25/C revealed a mass activity of 203 mA mgPt −1 (in 0.5 M HClO 4 at 0.9 V). Li et al. [18] observed that PtCo/C nanoparticles have a size of 4.7 nm, showing a maximum ORR mass activity of 270 mA mgPt −1. Although there are many reports regarding PtCo/C catalysts, such as those mentioned above, it is necessary to prepare PtCo/C with a simple method that can be easily scaled up in the future.

The polyol method is always used to prepare Pt/C electrocatalysts because of its simplicity and the use of simple solvents such as ethylene glycol (EG) [18]. However, when preparing Pt/C electrocatalysts with high Pt loading (40 wt%), modification of the
polyol method is often used to tune Pt nanoparticles sizes to obtain a narrow distribution in the range of 1–5 nm. Song et al. [19] studied Pt (50 wt%) supported on XC-72R that was prepared by a conventional polyol method with pulse-microwaving using an EG solvent, which was also acting as a reducing agent. The size of the Pt nanoparticles was approximately 2.7 nm due to the fast reduction process. The results showed that Pt/C 50 wt% could exhibit ORR activity as much as commercial electro catalysts. Their preparation method could result in better electrocatalytic performance compared with conventional reduction by the NaBH4 method. Normally, most polyol methods are quite complicated and expensive—especially preparing Pt/C electrocatalysts with high Pt loading (>40 wt%). A stabilizing agent or an additive is usually utilized to inhibit Pt nanoparticle agglomeration. The use of an additive could lead to additional procedures for synthesis processes such as introducing removing agent(s), which could stay in the catalysts and poison them [20]. It is essential to introduce a new method for the use of additive agents that can be removed smoothly, without the addition of more complex process.

An EG mixture in aqueous form was used as a substitute for pure EG to make PtCo/C as a catalyst. Firstly, water was used to dilute the EG; this was to control the rate of Pt reduction in the reaction and the distribution of the tune size, and then to prevent the agglomeration of Pt nanoparticles. Secondly, the addition of water is good for EG removal during PtCo/C purification because pure EG is easily trapped in the pores of carbon, due to its high viscosity—this could make the washing out process difficult. The characterization of structure and electrochemical measurements were performed to study the effects of EG/water on the structure and electrochemical specifications of PtCo/C catalysts. A PtCo/C catalyst was produced without a protective agent, with a mass activity of 304 mA mgPt−1. The increased electrocatalytic activity showed that the synthesis strategy developed here was practical and could be used for the preparation of ORR electrocatalysts.

2. Results and Discussion
2.1. Structural Characterization

Figure 1 shows the XRD patterns for the PtCo/C and commercial Pt/C-JM catalysts obtained from Johnson Matthey. It can be seen that all the carbon-supported Pt catalysts showed two main characteristic peaks (Pt(200) and Pt(111)), which were in good agreement with the peaks obtained from some other papers, indicating that the Pt precursor was reduced (in modified polyol solution) by the use of EG (as solvent and reduction agent). In the case of the PtCo/C catalysts, the XRD patterns also exhibited two main characteristic peaks that were slightly right-shifted compared to the Pt/C catalysts due to the formation of Pt–Co alloys. It was observed that after the formation of the Pt–Co alloys, the (111) peak of the Pt–Co alloys moved to between the Pt(111) peak of pure Pt and the Co(111) peak of pure Co, while the (200) peak of the Pt–Co alloy fell in between the (200) peak of pure Pt and the (200) peak of pure Co. No other peaks were seen for the metallic CoO or Co—indicating successful alloying and the reduction of the Co(II) precursor to metallic Co with Pt with the method used. The Deby–Scherrer equation was used to calculate all the crystallite sizes of the Pt–Co alloys, as shown in Table 1.

![XRD patterns of the commercial Pt/C(JM) and prepared PtCo/C catalysts.](image)
Table 1. Property comparison for the commercial Pt/C(JM) and prepared PtCo/C catalysts.

| Sample         | Crystallite Size (nm) \(^a\) | Particle Size (nm) \(^b\) | Pt:Co (Real Atomic Ratio) \(^c\) |
|----------------|-------------------------------|--------------------------|-------------------------------|
| Commercial Pt/C | 4.3                           | 4.1 ± 0.5                | /                             |
| Prepared PtCo/C | 4.6                           | 4.8 ± 0.5                | 3:1                           |

\(^a\) Estimated from XRD data using the Scherrer formula. \(^b\) Obtained from TEM measurements. \(^c\) Based on EDX analysis.

Typical TEM images of the PtCo/C and Pt/C-JM catalysts are presented in Figure 2, in which the particle sizes are displayed and their average values are shown in Table 1. The data for the PtCo/C and Pt/C-JM catalysts from the literature are also shown in Figure 2c and Table 1. The formation of Pt–Co alloys could result in increases in the size of the nanoparticles. The crystallite sizes were basically in accordance with the sizes calculated from the TEM images. The PtCo/C nanonparticle size was under 5 nm, showing its high ORR activity potential.

![TEM images](image_url)
The XPS peaks of the 4f and 2p orbitals for the Pt and Co can be observed in Figure 3, respectively. In comparison with the Pt/C-JM, a slight shift in Pt 4f\textsubscript{7/2} can be seen for the PtCo/C catalysts due to the presence of alloying. From the XPS analysis, the surface Pt/Co atomic ratios were about 3:1. Higher ratios were obtained from the XPS results, but only with a depth of 2–3 nm.

![Figure 3. XPS spectra for the commercial Pt/C(JM) and prepared PtCo/C catalyst: Pt 4f (a) and Co 2p (b); deconvoluted Pt 4f (c,d).](image)

It can be observed that after the leaching, the Co content of the leached Pt–Co alloys decreased significantly, which indicates that the Co atoms were partly removed. The XPS analyses showed higher surface ratios for atomic Pt/Co compared to those determined by the EDX analyses, which demonstrates that Co atoms were separated from the PtCo alloy surface. As a result, for the leached PtCo/C catalysts, a Pt-skin/PtCo skeleton configuration was used. A Pt-skin configuration could provide protection for PtCo alloy nanoparticles and also increase the electrochemical stability of the PtCo/C alloy. Additionally, it could improve the electrocatalytic activity of the ORR. An ideal pure Pt skin layer cannot be easily and practically obtained for fuel cell catalysts.

2.2. Electrochemical Studies

Figure 4 presents the CV profiles for the PtCo/C and Pt/C-JM electrocatalysts under the testing conditions. The curves of the PtCo/C exhibited voltammetric peaks in the range of +0.6 to 1.0 V, resulting from the formation of Pt oxide in the anodic scan and also the Pt oxide reduction in the opposite sweep. After leaching the Co, no Co on the surface of PtCo/C was observed—showing that the Pt-rich surface played a critical role in the cyclic voltammetry curves. After accelerated durability testing (ADT), the CV curve of the leached PtCo/C samples showed a tendency to shrink due to the decline in electrochemical stability.
Investigation of the stability of the PtCo/C for the ORR was carried out at a constant potential scan rate of 5 mV/s. The stability measurement was conducted after running accelerated durability testing (ADT, continuous potential cycling for 100 cycles between 0.6 and 1.2 V vs. RHE (reversible hydrogen electrode) at a potential scan rate of 50 mV/s in a N2/purged 0.1 M HClO4 solution).

The ORR activity of the PtCo/C and Pt/C-JM catalysts electrodes was also monitored by liner sweep voltammetry (LSV) measurements under O2/saturated/0.1 M HClO4 at 10 mV/s with a rotation rate in the range of 400 to 2500 rpm, as shown in Figure 5. For PtCo/C electrocatalysts, the half-wave potential was 0.90 V. In comparison with the 20% Pt/C-JM (at the same loading condition-onset potential of 0.902 V), the PtCo/C manifested a comparable ORR performance. The good ORR performance of the PtCo/C was identified by the cathodic current density, which was obtained at 0.8 V (as presented in Figure 6). The cathodic current density PtCo/C was 5.36 mA/cm², 112% higher than that of the 20 wt% Pt/C-JM.

Figure 4. Cyclic voltammograms for the prepared PtCo/C (a) and commercial Pt/C(JM) (b), catalyst before and after ADT in N2/saturated 0.1 M HClO4 solution at a scan rate of 10 m V/s. The stability measurement was conducted after running accelerated durability testing (ADT, continuous potential cycling for 100 cycles between 0.6 and 1.2 V vs. RHE (reversible hydrogen electrode) at a potential scan rate of 50 mV/s in a N2/purged 0.1 M HClO4 solution).

Figure 5. Liner sweep voltammetry (LSV) for oxygen reduction of the commercial Pt/C(JM) (b) and prepared PtCo/C (a) catalyst in O2/saturated 0.1 M HClO4 solution at different rotation speeds and scan rate of 5 mV/s.
Investigation of the stability of the PtCo/C for the ORR was carried out at a constant potential (0.75 V) by chronopotentiometry (Figure 7). The PtCo/C manifested excellent stability for the ORR, which attained a current density of 4.3 mA/cm² all through the start point—subsequently reaching 4.2 mA/cm² after 10,000 s, which could suggest that the current density was almost stable. It could also demonstrate the excellent performance of the PtCo/C electrode as a low-platinum metal catalyst with superior ORR activity.

![Figure 6.](image)

**Figure 6.** Half-wave potential of the Pt/C(JM) and prepared PtCo/C catalysts (a); exchange current density of the Pt/C(JM) and prepared PtCo/C, tested at 0.8 V (b); in an O₂/saturated 0.1 M HClO₄ solution with a 2500 rpm rotation rate at a 10 mV/s scan rate.

![Figure 7.](image)

**Figure 7.** Current-time chronoamperometric response for the commercial Pt/C(JM) and prepared PtCo/C catalyst under 1600 rpm in O₂/saturated 0.1 M HClO₄ solution at 0.75 V(b).

3. Experimental Materials and Methods

3.1. Raw Chemicals

1 M NaOH solution, perchloric acid (HClO₄, 70 wt%, ACS reagent, sigma Aldrich, Saint Louis, MO, USA), Crobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98%, ACS reagent, sigma Aldrich, Saint Louis, MO, USA), iso-propyl alcohol, Chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, ACS reagent, sigma Aldrich, Saint Louis, MO, USA), carbon black (VXC-72, CABOT), high purity N₂ (99.9%) and high purity O₂ (99.9%) were consumed as received. A commercial carbon-supported platinum catalyst (40 wt% Pt) was obtained from Johnson Matthey (Pt/C-JM).

3.2. Preparation Methods

A modified polyol method using EG and water as solvents was used to obtain 50 wt% Pt/C catalysts. An optimum amount of carbon was added to 25 mL of EG/23 mL of water.
using a flask (250 mL) and was sonicated at 300 KW (for 1 h) at room temperature to obtain the carbon suspension. Then, in a container, a calculated amount of Co(NO$_3$)$_2$ and H$_2$PtCl$_6$ was added into 25 mL of EG. The mole ratio of the Pt and Co was 3:1. After being sonicated (for 10 min), H$_2$PtCl$_6$ and Co(NO$_3$)$_2$ solutions were added into the suspension of carbon in the flask with continuous stirring. After 30 min, the pH was adjusted to 10, which was kept constant using NaOH (1 M). The temperature of the mixture was increased to 160 °C (under reflux) and was kept unchanged for 3 h. Then, the mixture temperature was reduced to 40 °C and the pH was adjusted to 2. Finally, the temperature was kept at 40 °C for 20 h. The mixture was infiltrated and washed with de-ionized water to reach a pH of 7. To remove the solvent, the product was dried at 55 °C for 24 h. For comparison, commercial carbon that included a supported platinum catalyst, was utilized as a reference catalyst labeled Pt/C-JM.

### 3.3. Characterization

The powder was analyzed by an X-ray diffractometer (XRD, Bruker D8 Advances, Munich, Germany). Cu Kα (λ = 1.5406 Å) between 20° and 90° was used. An ESCALAB 250Xi instrument from Thermo Fisher (Waltham, MA, USA) was used to test the X-ray photoelectron spectroscopy (XPS). The XPS spectra reference was C 1s with 284.5 eV binding energy. TEM and elemental mapping (Titan G2 60-300, FEI, Hillsboro, USA) were used to test the particle size of the PtCo/C electrocatalysts.

Electrochemical tests were performed by Gamry from the USA. For this aim, 5 mg of active material was poured into a solution of 1 mL ethanol nafion composite with nafion: ethanol = 1:9 to obtain uniform inks, with dipping on a glass carbon disc surface electrode. Pt foils with dimensions of 3.0 cm$^2$ were used as counter electrodes, and saturated calomel electrodes (SCEs) were used as the reference electrodes. The ORR activity of the electrodes was measured by cyclic voltammetry (CVs) in oxygen-saturated 0.1 M HClO$_4$ (scan rate 50 m V/s, rotating rate 1600 rom) and nitrogen with a flow rate of 20 mL/min at room temperature. The catalyst loading was 10 µL. Linear sweep voltammetry (LSV) was used to analyze the ORR activity at 10 mV/s (in oxygen 0.1 M HClO$_4$). The rotating rates for the catalyst loading (10 µL) were set from 400 to 2500 rpm. Chronopotentiometry curves were used at a current density of 3 mA/cm$^2$. For comparison, Pt/C-JM was used for the ORR under the same conditions.

### 4. Conclusions

An easy preparation method for PtCo/C electrocatalysts was adopted using heat-treatment, and chemical de-alloying as the next stage. EG and water were utilized as the solvent and reducing agent. The PtCo/C electrocatalysts were one of the best low-platinum precious metal catalysts, exhibiting an onset potential of 0.98 V and a half-wave potential of 0.831 V—similar to those of the Pt/C catalysts. These results may indicate the possibility of PtCo/C catalyst applications at a large scale for PEM fuel cells due to the simplicity of their synthesis process.

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