

Novel synthesis of highly active Pt/C cathode electrocatalyst for direct methanol fuel cell

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A 40 wt% Pt/C cathode electrocatalyst with controlled Pt particle size of ~2.9 nm showing better performance than commercial catalyst for direct methanol fuel cell was prepared by a polyol process with water but without using stabilizing agent.

Pt-based electrocatalysts with high loading are usually employed in direct methanol fuel cells (DMFC) as cathode electrocatalysts for oxygen reduction reaction at relatively low temperature. Synthesis of highly dispersed supported platinum with uniform nanoparticle size still remains a challenge, especially for high metal loading. The conventional methods for the synthesis of Pt and Pt alloy electrocatalysts are mainly impregnation¹ and colloid methods such as sulfite-complex route² and NR⁴⁺-stabilized metal colloids route.³ The impregnation is limited because the average particle size is usually large and the size distribution is broad. Both colloidal routes produced well-homogenized ultrafine Pt electrocatalysts, but the complexity of these synthesis hinders its utilization.⁴ Many investigators have contributed much endeavour to search for alternative routes.⁵ In this paper, uniform platinum nanoparticles with an average diameter of about 2.9 nm supported on carbon with Pt loading up to 40 wt% were prepared by a modified polyol process. The modified polyol method exhibits the merits of impregnation and colloid procedures, *i.e.*, the preparation method is simple but it is able to control the particle size and distribution. The as-synthesized Pt/C electrocatalyst shows better electrocatalytic activity for oxygen reduction reaction in DMFC than that of the commercial catalyst.

The precursor, chloroplatinic acid, was dissolved into ethylene glycol (EG) and mixed with carbon black (Vulcan XC-72R, Cabot Corp., $S_{\text{BET}} = 236.8 \text{ m}^2 \text{ g}^{-1}$) suspended in distilled

water. The mixture was maintained at 403 K in an oil bath for 3 h to ensure the complete reduction of Pt. A flow of argon was passed through the reaction system to remove oxygen and organic by-products. In the course of reaction, the evolved vapour was trapped and collected for GC-MS analysis. The resulting solid was filtered, washed with copious distilled water and dried at 343 K *in vacuo*. The obtained sample was denoted as 40 wt% Pt/C-EG.† The obtained electrocatalyst contains no stabilizing agent. This feature makes the modified process unique, because applications of the traditional polyol process⁶ based on stabilizer such as polyvinyl pyrrolidone (PVP) were restricted in the area of electrocatalysis due to serious agglomeration of metal particles after removing the surfactant at relatively high temperature. Besides, the modified polyol process is carried out in a EG/H₂O mixed solution, whereas, for the conventional polyol process, a strictly anhydrous organic solution is required.⁶ The 40 wt% Pt/C-EG and the commercial 40 wt% Pt/C (Johnson Matthey Corp., denoted as 40 wt% Pt/C-JM) were comparatively tested as cathode electrocatalyst in DMFC.

Fig. 1a shows the TEM image of the 40% Pt/C-EG sample. As the image shows, the spherical platinum particles on carbon are uniform and well distributed. Based on the measurements of 300 particles in random regions, the average particle size was estimated to be 2.9 nm. The corresponding histogram (Fig. 1b) reveals that the particle size distribution is rather narrow and exhibits the features of a log-normal distribution. Chemisorption of CO was carried out in the flow of He at ambient temperature to confirm the TEM results. Prior to chemisorption, the samples were reduced under H₂ flow at 120 °C for 1 h. As demonstrated in Table 1, the CO chemisorption results were consistent with TEM results. These different measurements

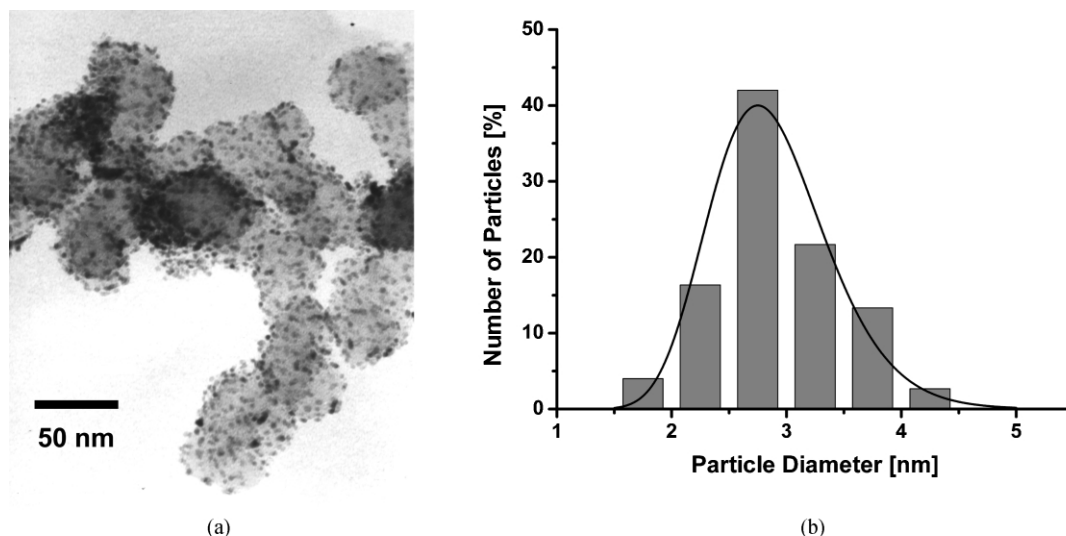
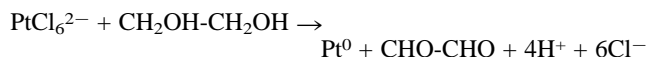


Fig. 1 TEM analysis of 40 wt% Pt/C-EG with 20,000 magnifications: (a) TEM image, (b) corresponding particle size distribution.

identically show that the average platinum particle size of 40 wt% Pt/C-EG is smaller than that of the commercial 40 wt% Pt/C-JM.

Surprisingly, our detailed investigations find that the metal particle size and distribution strongly depend on the sequence of water addition. When water is dropped into the solution of chloroplatinic acid dissolved in EG at up to 50% V/V, small metal particles are formed whether the metal is supported or unsupported; *vice versa*, the aggregation of particles takes place and usually large metal particles are observed. Therefore, the size of platinum particles could be controlled by changing the water content in the starting reaction system.

UV-Vis spectroscopy measurement showed that the typical absorption of Pt⁴⁺ at 264 nm⁷ completely disappeared when the EG/water (v/v = 1/1)-dissolved chloroplatinic acid was placed in a water bath at 100 °C for only 2 min. The disappearance of the absorption at 264 nm was shortened to 16 s when the reaction system was heated under microwave irradiation.[‡] In both cases, the absorption at 500 nm was observed and the colour of sol changed from yellow to black brown. These phenomena suggest the reduction reaction of Pt⁴⁺ is very quick under these conditions. Therefore, it is possible that the modified process can effectively control particles size and distribution under these operating conditions because of its fulfilment of two conditions: quick nucleation and a complete separation of the nucleation and growth steps.⁸ In addition, in both cases, there is no detectable absorption at 220 nm that is ascribed to Pt²⁺.⁷ *In-situ* NMR analysis of ¹⁹⁵Pt in the solution shows the existence of only Pt⁰ when the temperature of reaction system is raised to 75 °C, and glyoxal in the products has been detected by GC-MS. Therefore, this synthesis may follow a one-step reaction mechanism when the redox reaction operates under these conditions, namely:



The electrochemical performance tests of the 40 wt% Pt/C-EG and the commercial 40 wt% Pt/C-JM were made with a 30 × 30 mm single cell as cathode electrocatalysts under the same operation conditions. The preparation of membrane electrode assemblies (MEAs) and operation conditions of single-cell fuel cell have been described previously.⁹ As illustrated in Fig. 2, the single cell with the 40 wt% Pt/C-EG catalyst exhibited better performance than that of 40 wt% Pt/C-JM. The voltages are 0.70 V and 0.66 V at open circuit and 0.45 V and 0.39 V at 200 mA cm⁻² for 40 wt% Pt/C-EG and 40 wt% Pt/C-JM, respectively. Apparently, high dispersion of platinum on carbon achieved a much higher electrocatalytic activity for oxygen reduction, indicating that the mass activity of the electrocatalyst increases with increasing the ratio of surface metal atoms. The crystallite size effect reported previously¹⁰ is not observed in this work. On the other hand, uniform distribution of the metal particles on the carbon support is also an important factor in improving the electrocatalytic activity.¹¹ A reasonable interpretation for the promotion is that the optimal interparticle distance can be obtained for the electrocatalyst with uniform distribution.¹² It is noteworthy that good performance is obtained in the presence of considerable polarization losses due to methanol crossover, in which highly dispersed Pt/C electrocatalysts also promote methanol oxidation in cathode even more than that of poorly dispersed Pt/C. Therefore, it is very important to develop methanol-tolerant oxygen reduction catalysts.¹³

Table 1 Particle size obtained from the different characterizing methods^a

Samples	TEM	CO-Chemisorption
40 wt% Pt/C-EG	2.9	3.3
40 wt% Pt/C-JM	3.8	4.0

^a The unit is nm.

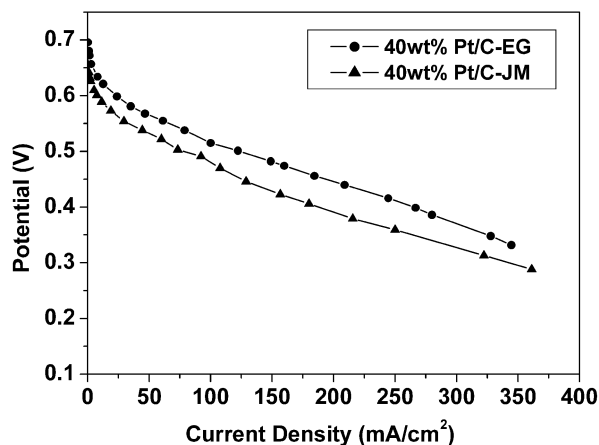


Fig. 2 Comparison of the performance of single cell adopting 40 wt% Pt/C made in-house and Johnson Matthey Corp. as cathode electrocatalysts. Operation temperature: 90 °C; methanol concentration: 1 mol L⁻¹; flow rate: 1 ml min⁻¹; oxygen pressure: 0.2 Mpa; noble metal loading in anode: 2 mgPtRu cm⁻² (20 wt% Pt-10 wt% Ru/C, Johnson Matthey); noble metal loading in cathode: 1 mgPt cm⁻² electrode membrane: Nafion-115.

In conclusion, this modified polyol process is simple and practical for the synthesis of highly dispersed Pt-based electrocatalysts with a narrow size distribution in the presence of high loading. The as-synthesized Pt/C electrocatalyst shows better electrocatalytic activity for oxygen reduction reaction in DMFC than that of the commercial catalyst.

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Notes and references

[†] The content of platinum was 40 wt% as determined by atomic absorption spectroscopy (AAS).

[‡] The 30 ml of EG/water (v/v = 1/1)-dissolved chloroplatinic acid irradiated with a microwave oven (National NN-S568WFS, 2450 MHz, 900 W).

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