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Synthesis of highly dispersed Pt/C electrocatalysts in ethylene glycol using acetate stabilizer for methanol electrooxidation

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Abstract

Pt/C electrocatalysts were prepared from a solution of H_2PtCl_6 in ethylene glycol in the presence of XC-72 carbon by adding a small amount of sodium acetate as stabilizer. Repeated TEM images showed that the platinum nanoparticles were small and uniform in size and highly dispersed on XC-72 carbon supports when a small amount of sodium acetate solution was added to the synthesis solution. The Pt/C electrocatalysts exhibited very high electrocatalytic activity for liquid methanol oxidation. The effects of adding acetate on Pt particle size and size distribution are discussed. It is demonstrated that acetate can be used as a good stabilizer for preparing Pt/C catalyst with fine and uniform Pt particles.

1. Introduction

Pt and Pt-based alloys are catalytically active in several room temperature electro-oxidation reactions of interest to fuel cell applications. Conventional methods for preparing Pt/C electrocatalysts are mainly based on the impregnation–reduction route and colloid methods. Impregnation is limited because the average particle size is usually large and the size distribution is broad. The colloidal routes produce well-homogenized ultrafine Pt electrocatalysts, but the complexity of these synthesis methods hinders their utilization. It is well known that the metal catalytic activity is strongly dependent on the particle shape, size and the particle size distribution. It was reported that Pt particles with about 3.0 nm exhibited higher mass electrocatalytic activity for oxygen reduction [1, 2], and PtRu particles with about 3.0 nm displayed highest mass catalytic activity for methanol electrooxidation [3]. Therefore, metal particles with high electrocatalytic activity should have suitable and uniform size. Synthesis of highly dispersed supported Pt particles with small and uniform size remains a challenge for preparing high-performance catalysts for fuel cell application. Many efforts have recently been made to develop alternative methods for preparing Pt and Pt-based alloys electrocatalysts, such as micro-emulsion [4], microwave irradiation [5], polyol process [6], microwave assisted polyol process [7, 8] and two-step spray pyrolysis process [9].

The polyol process has been proved to be an effective method for preparing colloidal metal particles [10, 11]. In this process, liquid ethylene glycol was commonly used as solvent for the metal salts, reducing agent, and growth medium for the metal particles. When the ethylene glycol solution containing the metal salt is refluxed at 160–180 °C, the metal ions are reduced to their elemental states. In order to avoid metal particle agglomeration, polymers, especially polyvinyl pyrolidine (PVP), have been employed as protective agents in the conventional polyol process [12–15]. However, the polymer stabilizers must be removed at relatively high temperature in the area of the electrocatalyst [16]. Because heat treatment causes agglomeration of metal particles and alters the properties of the catalysts, the polyol process using polymers as stabilizers has limited use in the synthesis of electrocatalysts.

Electrostatic stabilization is an alternative method of obtaining colloidal metal particle dispersions in solution. The citrate anion has been used as stabilizer to prepare noble metal nanoparticles such as gold [17], palladium [18], silver [19] and platinum [20]. Recently, sodium acetate was also found to be a good stabilizer for preparing Pt and Ru nanoparticles in the liquid polyol process [21, 22]. These carboxylic anions used as stabilizers were possibly preferred to polymer stabilizer for the synthesis of electrocatalysts because the anions were easily removed by washing with deionized water at room temperature. In the present work, we present a modified polyol process to synthesis highly dispersed Pt/

C electrocatalysts in ethylene glycol solution by adding a small amount of acetate as stabilizer. The effects of adding acetate on Pt particles size and size distribution were investigated. It was found that the Pt/C catalysts prepared by this modified method have highly dispersed and uniform Pt nanoparticles with average size of about 2.9–3.4 nm, and exhibited very high electrocatalytic activity for methanol electrooxidation.

2. Experimental

2.1. *Preparation and characterization of Pt/C electrocatalysts*

All chemical reagents were of analytical grade and used as received without purification. Vulcan XC-72 carbon with a specific surface area (BET) of 240 m^2 g^{-1} and an average particle size of 40 nm was also used as received. In a typical procedure, 2.0 ml solution of 0.05 mol l^{-1} $H_2PtCl_6 \cdot 6H_2O$ in ethylene glycol and 0.25 or 0.7 ml 1.0 mol l^{-1} sodium acetate solution were added to 100 ml ethylene glycol, and then were uniformly mixed with 80 mg Vulcan XC-72 carbon in an ultrasounic bath. The mixture was refluxed at 170 °C in an oil bath for 3 h to ensure complete reduction. The resulting suspension was filtered and the residue was washed with acetone and copious amounts of deionized water and the acetate ions was removed. The solid product was dried at 100 °C for 12 h in a vacuum oven. The normal mass percentage of Pt in the Pt/C catalysts is 20% in this work.

The metal contents were determined by energy dispersion X-ray spectrum analysis (EDX) on a JEOL JSM-5600LV scanning electron microscope. XRD patterns were obtained on a Philips PW diffractometer equipped with a CuKα as radiation source (λ = 0.15406 nm) and operating at 40 kV and 40 mA. TEM images were recorded on a JEM-200CX transmission electron microscope with an accelerating voltage of 160 kV. Sample preparation for TEM examination involved the ultrasonic dispersion of the sample in ethanol and placing a drop of the suspension on a copper grid covered with a perforated carbon film.

2.2. *Electrochemical characterizations of Pt/C electrocatalysts for methanol oxidation*

A CHI 660B potentiostat/galvanostat and a three-electrode test cell were used for cyclic voltammetry and chronoamperometry experiments of methanol electrooxidation on a Pt/C catalyst electrode at 30 °C. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The working electrode was a thin layer of Nafion-impregnated Pt/C catalyst cast on a glass carbon disk with 4.0 mm diameter held in a Teflon cylinder. The catalyst layer was obtained in the following way: a slurry was first prepared by sonicating a mixture of 500 mg of deionized water, 10 mg of Pt/C catalyst and 200 mg of Nafion solution (Aldrich, 5% Nafion); then 2.0 μl of the slurry was pipetted and spread on the glass carbon disk. The electrode was finally dried at 80 °C for 10 min. The electrolyte was an aqueous solution of 2 mol l^{-1} CH_3OH in 1 mol l^{-1} H_2SO_4. All electrolyte solutions were deaerated by high purity nitrogen for 30 min prior to electrochemical measurements.

3. Results and discussion

Repeated EDX measurements showed that the Pt mass percentage of the Pt/C catalysts prepared in ethylene glycol solution adding acetate as stabilizer ranged from 18.7 to 20.3%, which are agreed with the ratio of Pt to carbon support in the starting mixture. XRD patterns of the Pt/C catalysts are shown in Figure 1. The wide diffraction peak at $2\theta = 25.1°$ is attributed to the graphite structure (002) of XC-72 carbon supports due to the larger interplanar spacing of XC-72 carbon (d_{002} = 0.355 nm). The diffraction peaks at $2\theta = 39.8°$ (111), 46.4° (200) and 67.8° (220) due to Pt nanoparticles can be indexed to face-centered cubic platinum, which is consistent with the standard powder diffraction file of Pt (JCPDS No. 04-0802). The diffraction peak at $2\theta = 39.8°$ for Pt (111) corresponds well with the interplanar spacing of d_{111} = 0.227 nm.

In order to examine the effects of adding acetate on the Pt particle size and size distribution of Pt/C catalysts, the samples were characterized by TEM imaging. TEM images and a histogram of Pt nanoparticle size distributions are shown in Figures 2 and 3, respectively. The Pt nanoparticles had a larger mean size and a broad size distribution when no acetate was added to the synthesis solution. The mean size was 4.5 nm with the size distribution ranging from 1.0 to 8.0 nm. When a small amount of acetate was added to the synthesis solution, the Pt nanoparticles became small and

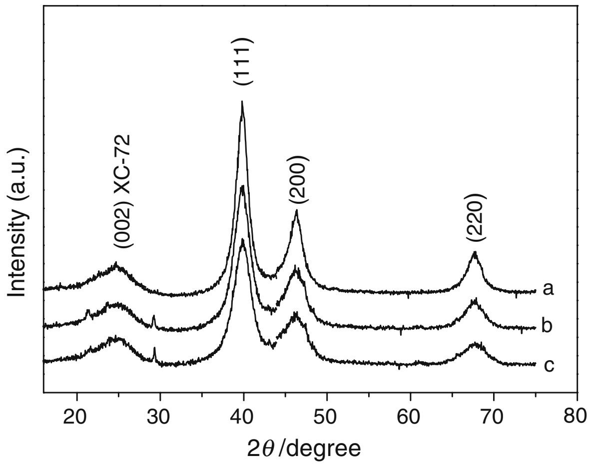

Fig. 1. XRD patterns of Pt/XC-72 catalysts prepared in ethylene glycol solution by adding (a) 0.0 ml, (b) 0.25 ml and (c) 0.70 ml of 1.0 mol l^{-1} acetate solution as stabilizer.

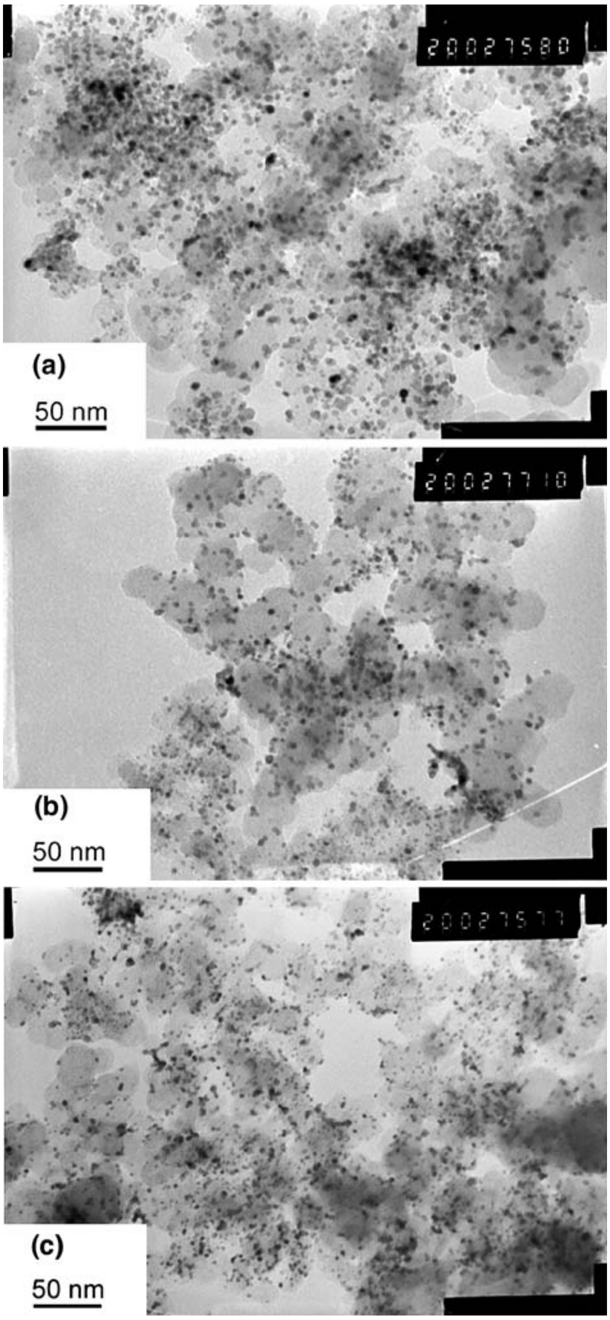

Fig. 2. TEM images of Pt/XC-72 catalysts prepared in ethylene glycol solution by adding (a) 0.0 ml, (b) 0.25 ml and (c) 0.70 ml of 1.0 mol l^{-1} acetate solution as stabilizer.

uniform. When 0.25 ml of 1.0 mol l^{-1} acetate solution was added into 100 ml of the synthesis solution, the mean size of Pt nanoparticles was 3.4 nm with a size distribution ranging from 1.5 to 6.0 nm. When 0.70 ml of 1.0 mol l^{-1} acetate solution was added, the mean size was 2.9 nm with a size distribution ranging from 1.0 to 5.5 nm. Moreover, 89% of the Pt particles ranged from 2.0 to 4.0 nm, as shown in Figure 3(c), with only few particles larger than 4.0 nm or lower than 1.5 nm. The above facts indicate adding a small amount of sodium acetate solution as stabilizer constructs a good method for preparing highly dispersed and uniform Pt/C catalyst in liquid polyol solution.

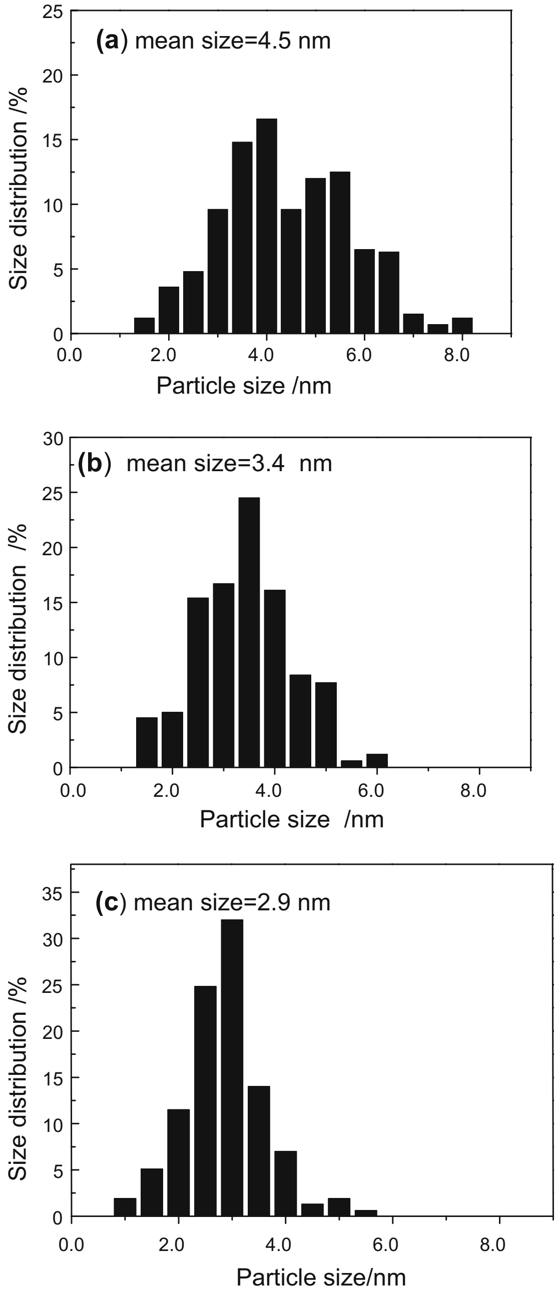

Fig. 3. Histogram of Pt nanoparticle size distribution of Pt/XC-72 catalysts prepared in ethylene glycol solution by adding (a) 0.0 ml, (b) 0.25 ml and (c) 0.70 ml of 1.0 mol l^{-1} acetate solution as stabilizer.

Noble metal colloids such as Pt, Ag, Ru and Pd have been prepared in ethylene glycol solution. However in a liquid-phase process, metal particles have a strong tendency to coalesce during their formation. In the traditional polyol process, polymers such as poly-vinyl-pyrrolidone (PVP) were commonly employed as steric stabilizers to avoid the agglomeration of metal particles [11–15]. The polymer stabilizer must be removed at relatively high temperature, but the heat treatment causes particle agglomeration [16]. Therefore, electrostatic stabilization is preferred to polymer stabilizers for electrocatalyst preparation. Citrate ions have been used

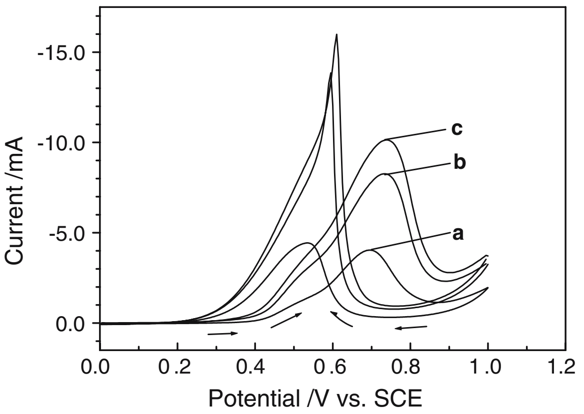

Fig. 4. Cyclic voltammograms of methanol eletrooxidation on Pt/C catalysts in 2 mol l^{-1} CH_3OH/1 mol l^{-1} H_2SO_4 electrolyte at a scan rate of 20 mV/s at 30 °C. The catalysts were prepared in ethylene glycol solution by adding (a) 0.0 ml, (b) 0.25 ml and (c) 0.70 ml of 1.0 mol l^{-1} acetate solution as stabilizer.

in aqueous colloidal solutions of Ag, Pd, Au, and Pt [17–20]. The acetate anion was also found to permit the formation of nonagglomerated Ru particles in polyols [23]. Recently, it was reported that fine and uniform Pt and Ru naoparticles could be prepared in liquid polyol by adding acetate [21, 22]. This means that acetate can be used as stabilizing agent for preparing nonagglomerated Pt and Ru nanoparticles with small and uniform size. The stabilizing function is due to the fact that acetate anions with metal particles can form chelate-type complexes via their carboxyl groups [21–23]. Because the acetate is easily removed by washing with deionized water at room temperature, it can be used as a good stabilizer for the synthesis of highly dispersed Pt/C electrocatalysts.

Figure 4 shows the cyclic voltammograms of methanol electrooxidation on Pt/C catalyst electrodes in the electrolyte of 2.0 mol l^{-1} CH_3OH/1.0 mol l^{-1} H_2SO_4 at 30 °C. The current peak at about 0.75 V vs. SCE in the forward scan is attributed to methanol electrooxidation. As shown in Figure 4, the current peak of methanol electrooxidation on Pt/C catalyst prepared in the synthesis solution without added acetate displays the lowest peak current. The low electrocatalytic activity is due to the large Pt average particle size and broad size distribution. The Pt/C catalysts prepared in the synthesis solution adding acetate as stabilizer display higher peak currents of methanol electrooxidation. The peak currents of methanol electrooxidation on the Pt/C catalysts prepared by adding acetate as stabilizer are about 200–250% that of Pt/C prepared without added acetate.

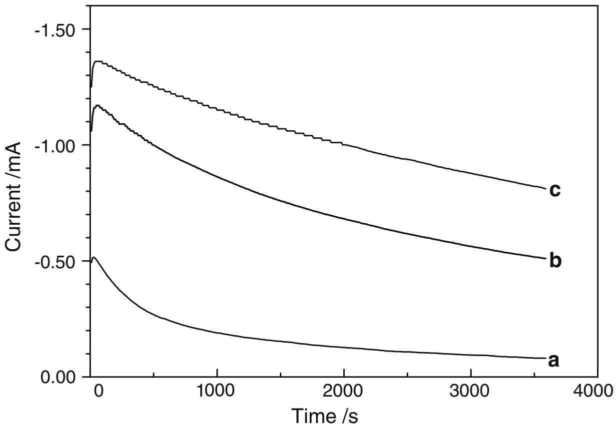

Fig. 5. Polarization current vs. time plots for the electrooxidation of methanol in 2.0 mol l^{-1} CH_3OH/1.0 mol l^{-1} H_2SO_4 electrolyte at 0.4 V (vs. SCE) at 30 °C. The catalysts were prepared in ethylene glycol solution by adding (a) 0.0 ml, (b) 0.25 ml and (c) 0.70 ml of 1.0 mol l^{-1} acetate solution as stabilizer.

The difference is significant enough that the current of methanol electrooxidation at 0.4 V vs. SCE can be used as an indicator of the activity of the catalysts under moderate polarization conditions. The Pt/C catalysts were therefore biased at 0.4 V vs. SCE and the changes in their polarization currents with time are shown in Figure 5. It can be seen that the current measured for the Pt/C catalysts prepared adding acetate as stabilizer exhibits higher polartization currents than that prepared with no added acetate. As shown in Figure 5, the initial polarization current is 0.52, 1.2 and 1.4 mA for the Pt/C catalyst prepared without acetate and with added 0.25 and 0.70 ml of 1.0 mol l^{-1} acetate solution. The current measured for Pt/C catalyst prepared without added acetate decreases continuously and eventually reaches only 16% of the initial current after 1.0 h. While the current measured for Pt/C catalyst prepared with acetate decreases moderately with time, and 44–60% of the initial value was salvaged after 1.0 h. We believed that the improvement in the catalyst performance derives directly from the fact that the Pt nanoparticles are small and uniform in size, and high dispersed on the carbon when acetate is added to the synthesis solution.

4. Conclusion

Highly dispersed Pt/C electrocatalysts with small and uniform size were successfully synthesized in ethylene glycol solution by adding a small amount of sodium acetate as stabilizer, without using surfactant or polymer stabilizer. The Pt/C catalysts prepared using this method exhibit high electrocatalytic activities for methanol electrooxidation. It is demonstrated that acetate can be used as a good stabilizer for directly preparing noble metal nanoparticles with small and uniform size supported on carbon in the liquid polyol process. The synthesis strategy presented here is simple and effective and provides a promising method for preparing carbon supported size-selected noble metal catalysts. In addition, since it has been reported that acetate can be used as stabilizer to synthesize other noble metal nanoparticles in polyol [17–23], the method presented in this work will be expected to prepare other supported noble metal and Pt-based alloy catalysts such as PtRu/C, which are more suitable for methanol electrooxidation due to their good tolerance for carbon monoxide poisoning.

Acknowledgments

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