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ELECTROCHIMICA

Electrochimica Acta 52 (2007) 7278-7285

www.elsevier.com/locate/electacta

Investigation of carbon-supported Pt nanocatalyst preparation by the polyol process for fuel cell applications

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Received 10 March 2007; received in revised form 18 May 2007; accepted 29 May 2007

Available online 17 June 2007

Abstract

Parametric investigation of the polyol process for the preparation of carbon-supported Pt nanoparticles as catalysts for fuel cells was carried out. It was found that the concentration of glycolate anion, which is a function of pH, plays an important role in controlling Pt particle size and loading on carbon. It was observed that Pt loading decreased with increasing alkalinity of the solution. As evidenced by zeta potential measurement, this was mainly due to poor adsorption or repulsive forces between the metal colloids and the supports. In order to modify the conventional polyol process, the effect of the gas purging conditions on the characteristics of Pt/C was examined. By the optimization of the gas environment during the reaction, it was possible to obtain high loading of 39.5 wt% with a 2.8 nm size of Pt particle. From the single cell test, it was found that operating in ambient O₂ at 70 °C can deliver high performance of more than 0.6 V at 1.44 A cm⁻². © 2007 Elsevier Ltd. All rights reserved.

Keywords: Polyol process; Ethylene glycol; Zeta potential; PEM fuel cells

1. Introduction

There is tremendous interest in the preparation of carbonsupported electro-catalysts for fuel cell applications [1–4]. It is well known that the performance of catalysts can be improved by achieving nanosized particles, uniform distribution and high loading of catalysts over large surface area carbons [5–7]. Conventional preparation techniques used for the preparation of supported catalysts are based on the wet impregnation followed by reduction in a hydrogen atmosphere at high temperatures or the chemical reduction of the metal precursors using reducing agents. However, these methods do not provide adequate control of particle size and distribution. Many studies have shown the difficulty of high metal loadings without a significant increase in the particle size [8,9].

Extensive investigations have been carried out to develop alternate routes for preparing supported Pt catalysts by the colloidal method using diverse stabilizing agents. In those attempts, a stabilizing agent was used to prevent the aggregation of metal particles during the nucleation and growth steps. Boennemann et

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al. developed organoaluminum-stabilized colloids with a particle size smaller than 2 nm at room temperature [10]. Organic stabilizers such as polyvinyl pirrolidone (PVP) and the surfactant dodecyldimethyl (3-sulfo-propyl) ammonium hydroxide (SB12) are widely used in the preparation of metal colloids [2,11,12]. The intrinsic problem underlying this process is that the stabilizing organic material remains on the surface of metal colloids. This should be removed prior to the application of metal particles for electrocatalysis. Removal of the organic material is important as it hinders the access of fuel to the catalyst sites. In general, the removal of stabilizer involves heat treatment. Consequently, due to the sintering effect, the phase separation and the distribution of metal particles are affected, resulting in lowered catalytic performance.

In this respect, preparation via the polyol process is preferred due to several advantages. The polyol process is a technique in which a polyol such as ethylene glycol is used as both solvent and reducing agent. The polyol method has been used for the preparation of nanometal powder [13,14] and nanowires [15,16]. A unique property of the polyol process is that it does not require any type of polymer stabilizer. In the polyol process using ethylene glycol, metal ions are reduced to form a metal colloid by receiving the electrons from the oxidation of ethylene glycol to glycolic acid. Glycolic acid is present in its deprotonated

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form as glycolate anion in alkaline solution. It is believed that the glycolate anion acts as a stabilizer by adsorbing the metal colloids [17]. Furthermore, removal of these organics on the metal surface by heat treatment below $160 \,^{\circ}$ C has been reported, which is low enough to avoid the deleterious effects associated with heat treatment. However, no information is available on metal loading as a function of solution pH and different gas environment.

In the present work, a modified polyol process is utilized for nanosized Pt/C formation in different pH and gas environments. The aim of this study is to seek quantitative correlations between solution pH and metal loading on carbon. The effect of the gas environment during preparation steps on the variation of particle size and metal loading is examined.

2. Experimental

2.1. Preparation of Pt/C catalyst

A measured amount of PtCl₄ and NaOH were dissolved in 25 ml of ethylene glycol under vigorous stirring for 30 min. NaOH was introduced to adjust pH of solution. Since the pH is one of the crucial operating parameters in the polyol process it was precisely controlled and recorded at every step. After recording the initial pH of solution, the appropriate amount of carbon black (Ketjen black 300J) was added to solution to produce 40 wt% of Pt/C. The resulting suspension was stirred for 1 h at room temperature followed by heating under reflux at 160 °C for 3 h. The solution was allowed to cool down to room temperature and left for 12 h with continuous stirring. The pH of the solution was measured again and accepted as the final pH. The Pt/C particles in the solution were then filtrated and thoroughly washed with water. This carbon-supported Pt catalyst was dried in air for 1 h at 160 °C and a mortar was used to homogeneously grind the Pt/C catalyst material to powder. During each step of experiment, different gases (N₂, air and O₂) were supplied to create different atmospheres.

2.2. Characterizations

Cyclic voltammetry was used to determine the effective surface area of Pt catalysts and to calculate the particle size. The experiment was performed in 0.5 M H₂SO₄ at 25 °C saturated with nitrogen using a conventional three-electrode cell. A glassy carbon electrode with a thin film of prepared Pt/C catalyst was used as a working electrode. Platinum wire was used as a counter electrode and a standard Hg/HgSO4 electrode served as a reference electrode. The size and distribution of the Pt particles prepared by the polyol process was determined by using high resolution transmission electron microscopy (HR-TEM, JEM-30100 model). ICP-AES (Perkin-Elmer 4300DV) analysis was carried out to estimate the Pt loading over the carbon support. In order to understand the nature of the surface charge and explain the stability of the colloidal solution, the zeta potential (Malvern Instruments ZEN 3600) was measured for carbon black and the Pt particles individually as a function of solution pH. Powder X-ray diffraction scans (XRD) patterns of the catalysts were obtained using a Cu K α source operated at 40 keV at a scan rate of 0.033 s⁻¹.

2.3. Membrane electrode assembly (MEA) fabrication and cell operation

The cathode electrodes were prepared by ultrasonically blending a mixture of Pt/C catalyst, Nafion solution (5 wt%) from Aldrich) and isopropyl alcohol. The catalyst solution was then sprayed onto the surface of a single sided uncatalyzed gas diffusion layer obtained from E-TEK. The total loading of Pt was fixed at $0.4 \,\mathrm{mg}\,\mathrm{cm}^{-2}$ and the geometric active area of all MEAs was 5 cm². A commercial E-TEK electrode (30 wt% Pt/C, $0.5 \,\mathrm{mg}\,\mathrm{cm}^{-2}$) was used as the anode electrode in order to eliminate experimental errors that may originate from electrode preparation steps. Prior to the preparation of the MEA, a total of $0.8 \,\mathrm{mg}\,\mathrm{cm}^{-2}$ of Nafion solution was applied to the E-TEK anode electrode by means of the spray technique. Both anode and cathode electrodes with pretreated Nafion 112 membrane were hot-pressed at 140 °C for 3 min at a pressure of 3 tonnes to form MEA. The performance of the single cell was evaluated by measuring the current density versus cell voltage using a commercial test system (Wonatech). The reaction gases were supplied through a humidifier and a mass flow controller from hydrogen and oxygen tanks. The cell was operated under ambient pressure.

3. Results and discussion

Several reaction mechanisms of the polyol process are proposed in the literature. By using ethylene glycol in the presence of PVP, metallic particles are produced from the following reactions, as reported by Fievet et al. [18].

$$CH_2OH-CH_2OH \rightarrow CH_3CHO + H_2O$$
 (1)

$$2nCH_{3}OH + 2M^{n+} \rightarrow 2M + 2nH^{+} + nCH_{3}COCOCH_{3}$$
(2)

PVP acts as a capping reagent. However, there is a limitation on applying this mechanism in cases where PVP is not used. As shown by Bock et al. in the preparation of PtRu nanocatalysts [17], the reaction mechanism of the colloidal particle formation involves the interaction of -OH groups of ethylene glycol with Pt-ion sites resulting in the oxidation of the alcohol groups to aldehydes. These aldehydes are not very stable and undergo further oxidation to form glycolic acid and oxalic acid, respectively. These two carboxylic acids may again be oxidized to CO₂ or carbonate in alkaline media. The electrons donated by oxidation reactions result in the reduction of the Pt metal ions. This was supported by the fact that both oxalic and glycolic acids were detected in the HPLC analysis of the synthesis solutions. The quantitative analysis revealed that glycolic acid is the dominating product in the resulting solution. The dissociation constant of glycolic acid is known to be $1.48 \times 10^{-4} \text{ mol } \text{L}^{-1}$ at 25 °C [19]. This implies that glycolic acid is present in its deproto-



Fig. 1. Dependence of glycolate anion concentration as a function of pH.

nated form as the glycolate anion in alkaline solutions. Glycolate ion is considered to act as a stabilizer by forming chelate-type complexes via its carboxyl groups [17]. Consequently, a strong correlation has been drawn between the concentration of glycolate anion and particle size of metal in solution. The theoretical calculation of the glycolate anion concentration in the solution as a function of pH was carried out using the selected initial glycolic acid concentration and the dissociation constant. As shown in Fig. 1, the major change in the glycolate anion concentration was observed in the pH range of 2–6. A constant glycolate anion concentration was expected at pH higher than 6 and glycolate anion was absent from the solution at pH lower than 2. Based on the above estimation a Set of Pt/C catalyst samples was prepared by changing solution pH.

Fig. 2(a–f) shows the HR-TEM images of the Pt/C catalyst powder prepared by using (a) 0.00 M, (b) 0.05 M, (c) 0.075 M, (d) 0.1 M, (e) 0.15 M and (f) 0.2 M of NaOH, respectively. The influence of the NaOH concentration on the resulting final pH and Pt particle size determined from HR-TEM images are summarized in Table 1. Normally, the initial pH of solutions before refluxing was dropped as a result of the reduction of the Pt salts at higher temperatures. This drop in solution pH was consistent in all the solutions where NaOH was added. Therefore only the final pH is considered for discussion. According to Table 1, the final pH of the solution increases from 1.45 to 9.39 with increasing NaOH concentration in the solution. As shown in Fig. 2, it is observed that the Pt particle size decreases with an increase in NaOH concentration, whereas the effect is not so sig-

Table 1 Effect of NaOH concentration on the resulting Pt particles size and pH

NaOH (mol L ⁻¹)	Initial pH	Final pH	Particle size (nm) in XRD	Particle size (nm) in HR-TEM image 8.5	
0.0	0.72	1.45	5.2		
0.05	11.01	3.82	3.1	3.8	
0.075	11.73	4.33	2.1	3.1	
0.1	11.66	6.03	1.7	2.5	
0.15	11.75	8.50	1.7	2.3	
0.2	11.71	9.39	1.6	2.2	

nificant above 0.1 M of NaOH, which corresponds to pH 6.03. This result is in good agreement with those presented in Fig. 1. In the absence of glycolate ions where pH is 1.45, the Pt particle size is fairly large (~8.5 nm). Upon adding NaOH to the solution, the average Pt particle size decreases to 3.8 nm. This decrease in particle size is therefore attributed to the presence of glycolate ions in the solution resulting from the change in solution pH from 1.45 to 3.82. The stabilizing action of the glycolate ions helps in controlling the particle size. Upon increasing the concentration of glycolate ions in the synthesis solution by increasing the solution pH to 4.33 and 6.03, the Pt particle size is remarkably reduced down to 3.1 and 2.5 nm, respectively, as shown in Fig. 2(c and d). Upon further increase of the solution pH to 8.50 and 9.39, a marginal effect on the particle size was found as shown in Fig. 2(e and f). This is attributed to the fact that the concentration of glycolate anion is constant in this pH range. The particle size of Pt with different NaOH concentration was also confirmed with XRD patterns as shown in Fig. 3. The mean Pt particle sizes were calculated from Scherrer's formula based on Pt (111) peak and listed in Table 1. With increasing NaOH concentration, the diffraction peaks of Pt become broad which indicates a decrease in particle size. The particle size of Pt was remained constant after pH of 6 which was also observed from TEM analysis. These results strongly support the role of glycolate anion as a stabilizing agent.

Although a lot of work has been reported on the size control mechanism in the polyol process, few focused on the influence of metal loading on carbon as a function of the pH and synthesis conditions. In order to determine the Pt loading over carbon supports prepared by the polyol process, ICP-AES analysis was performed for the samples, as shown in Fig. 4. For the case where NaOH is not added to the solution, Pt loading on carbon support was measured to be 38 wt%, indicating that most of the Pt salts were reduced and loaded on carbon without a loss. Upon increasing the pH of the solution, the Pt loading decreased continuously and a rapid fall in Pt loading was observed at pH higher than 8.5. The presence of NaOH in the solution is helpful for controlling the particle size but the metal loading is seriously reduced. Pt is a precious metal and the production yield is really a catalyst cost benchmark.

In an attempt to explain this result, zeta potentials of Pt particles and carbons were measured as a function of pH separately, as illustrated in Fig. 5. Zeta potential is the potential difference, measured in the liquid, between the shear plane and the bulk of the liquid beyond the limits of the electrical double layer. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. In case of carbons, it is observed that the zeta potential changed to negative values with increasing pH. In aqueous media, the pH of the samples is one of the most important factors that affect the zeta potential. If carbons are placed in alkali media then the carbons tend to acquire more negative charge. The addition of acid causes a build up of positive charge. Therefore a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH. On the contrary, in the case of Pt particles, the zeta potential shifted to the negative direction when the pH increased up to 6, after which the zeta potential



Fig. 2. HR-TEM images of Pt particles on Ketjen black 300J prepared at different NaOH concentrations: (a) 0.0 M, (b) 0.05 M (c) 0.075 M, (d) 0.1 M, (e) 0.15 M and (f) 0.2 M. The bar indicates a 5 nm scale.

was not affected by the change in pH. The key thing to note is that pH 6 is the point where the concentration of glycolate anion starts to be saturated, as shown in Fig. 1. Based on this observation, it is reasonable to assume that there is a strong correlation between the concentration of glycolate anion and the zeta potential of Pt particles and that glycolate anions may be specifically adsorbed on the surface of a Pt particle, leading to a negatively charged surface. It is known that the stability of a colloidal is dependent upon the balance between the attractive van der Waals forces and the electrostatic repulsive forces between particles as they approach each other due to the Brownian motion they are undergoing [20]. Considering the values of zeta potential on both the species, it is concluded that the adsorption of Pt particles is higher when the charge of Pt colloids is opposite to that of carbon supports at low pH while the reduction of Pt loading with increasing pH of solution is caused



Fig. 3. XRD patterns of Pt/C prepared at different NaOH concentrations.



Fig. 4. The variation of Pt wt% deposited on carbon black as a function of NaOH concentration.



Fig. 5. Effect of changing solution pH on the zeta potential of Pt particles and carbon black.



Fig. 6. Cyclic voltammograms of the Pt/C catalysts prepared at different NaOH concentrations in 0.5 M $\rm H_2SO_4$ solution at 5 mV s^{-1}.

mainly by the electrostatic repulsive force between carbons and Pt particles.

Fig. 6 shows the cyclic voltammograms of Pt/C catalysts prepared at different solution pH. Since the total amount of Pt/C loaded on a glossy carbon electrode was constant, the actual content of Pt varied based on the Pt wt% in Pt/C samples. The CVs were recorded in 0.5 M H₂SO₄ as an electrolytic solution at a scan rate of 5 mV s^{-1} with N₂ purging. The effective surface area of the carbon-supported Pt nanoparticles was calculated from the area of the hydrogen desorption peaks between 0.03 and 0.3 V(SHE) after subtracting the contribution of the double layer charge. This area is converted into the effective active surface area of Pt using the conversion factor of $210 \,\mu C \,cm^{-2}$ [21]. The specific active surface area using the Pt wt% obtained from ICP analysis and the particle size, which was calculated from the specific active surface area based on the assumption of spherical shape of particle, are displayed in Fig. 7. As seen by the voltammograms, the area under the peak for hydrogen desorption increases with increasing pH as a consequence of an increasing active surface area of Pt nanoparticles, which are in accordance with the result of HR-TEM analysis.



Fig. 7. Specific active surface area and the particle size of Pt calculated from the cyclic voltammograms as a function of NaOH concentration.



Fig. 8. Effect of different gas environments on the Pt wt% and the final pH. The concentration of NaOH was fixed at 0.075 M.

As a controlling factor in the polyol process, the gas atmosphere of the reaction was also examined closely. The purpose of the experimental investigation of different gas modes is to find a method to increase the Pt loading on carbon without increasing the particle size of Pt. When N_2 or O_2 is purged in entire preparation steps, this is denoted as condition 1 and 2, respectively. For the case where the synthesis is performed under the open air environment, it is designated as condition 3. The last one, condition 4, is the mixed one. The reflux step at high temperature was carried out in N2 gas and the rest of process was performed in an open air environment at room temperature. In all the experiments the NaOH concentration in the solution was fixed at 0.075 M. Fig. 8 shows the effect of various gas atmospheres on the Pt loading and the final pH of the solution. Fig. 9 represents the corresponding HR-TEM images. It is interesting to note that during N₂ purging for condition 1, significantly reduced Pt loading (7 wt%) was obtained. It is likely that such small loading is associated with the difference in zeta potential and more probably the partial reduction of Pt ions. This is supported by the fact that the final pH of the solution prepared in condition 1 was much higher than those of the other conditions. Since the pH of the solution decreases as the reaction proceeds, this implies that the N₂ atmosphere suppresses the oxidation of aldehydes resulting in the lack of electron supply to reduce Pt ions completely. For condition 2, the particle size is relatively large with visible aggregates due to the low pH and 36 wt% of Pt loading was observed. The maximum Pt loading of 39.5 wt% was achieved for condition 4 with a particle size of about 2.8 nm. In order to initiate the oxidation of ethylene glycol, a reflux step at high temperature above 140 °C is required. However, it is not necessary to carry out the entire reaction at high tempera-



Fig. 9. HR-TEM images of Pt catalysts synthesized in ethylene glycol solution with different gas conditions: (a) N_2 purging, (b) open to air, (c) O_2 purging and (d) N_2 purging followed by opening to air. Spt is the specific active surface area calculated by cyclic voltammogram. The bar indicates a 5 nm scale.

Table 2
Kinetic parameters from regression analysis of polarization

Electrode	E^0 (V)	$b (\mathrm{V} \mathrm{dec}^{-1})$	$R(\Omega \mathrm{cm}^2)$	$i^0 (A cm^{-2})$	Roughness factor
0 M NaOH with air open	0.928	0.066	0.20	2.1×10^{-7}	70
0.075 M NaOH with N ₂ followed by air open	0.986	0.058	0.15	7.6×10^{-7}	265

ture since the oxidation of aldehydes is possible even at room temperature. Unlike conditions 2 and 3, condition 4 allows the reaction to take place at low temperature. It probably enables one to achieve a small Pt particle and high loading.

The performances of the MEAs in a single fuel cell are evaluated and shown in Fig. 10. From the results of Fig. 10, it is found that the electrode prepared at 0.075 M of NaOH with N_2 followed by open air (condition 4) shows much better performance in comparison to the electrode with 0 M of NaOH with open air (condition 3). This is attributed to the difference in particle size of Pt. As described before, the particle size is affected by the concentration of glycolate anion, which is a function of pH. In order to evaluate the electrode kinetic parameters from the polarization curves, the experimental data were fitted to the following semi-empirical equation [22]

$$E = E^0 - b\log i - Ri \tag{3}$$

$$E^0 = E_{\rm r} + b\log i^0 \tag{4}$$

where *E* and *I* are the experimentally measured cell voltage and current, E_r the reversible cell voltage, i^0 and *b* are the exchange current and the Tafel slope for oxygen reduction, respectively. *R* represents the total contributions of the linear polarization components, which include the charge transfer resistance of the hydrogen oxidation reaction, the resistance of the electrolyte in the cell and the linear diffusion terms caused by diffusion in the gas phase in the diffusion layer and/or in the thin film [23,24]. The regression results are summarized in Table 2. Both the electrodes show similar Tafel slopes of 66 and 58 mV dec⁻¹, which is close to the typical value of



Fig. 10. Comparison of MEA performance between the electrodes prepared at different NaOH concentrations and gas atmospheres.

 $60 \,\mathrm{mV} \,\mathrm{dec}^{-1}$ for Pt electrodes [25]. Note that the exchange current density of the electrode (0.075 M NaOH) is higher than that of the other electrode (0M NaOH). This is attributed to the difference in the roughness factor. Exchange current density is a measure of an electrode's readiness to proceed with an electrochemical reaction. For this reason, for an effective electrode, it is critical to maximize the exchange current density. The exchange current density of a fuel cell is generally expressed in terms of the geometrical surface area of the electrode rather than the actual surface area of the catalyst. Therefore, assuming that the nature of the oxygen reaction on Pt does not change, the magnitude of the exchange current density in fuel cells depends on the roughness factor, which is the ratio between the actual reactive surface area and the geometrical electrode area. Since the electrode prepared at 0.075 M has a higher active surface area, it ends up with a higher exchange current density.

4. Conclusions

An investigation of the parameters of Pt colloid synthesis using the polyol process was carried out. Although the adjustment of pH behaves as a key factor in controlling the nanodimension of the Pt particles, a severe reduction in the metal loading is observed with increasing solution pH. According to the zeta potential study, this is attributed to the electrostatic stabilization between Pt particles and carbon supports. The zeta potential of the carbon support decreased to negative values with increasing solution pH while that of the Pt particles remained constant at a negative charge after pH 6. Therefore, poor adsorption or repulsive forces between the metal colloids and the supports occurs, resulting in reduced Pt particle loading. Pt loading and particle size are also affected by the gas environment during Pt/C synthesis in the polyol process. It is observed that carrying out the entire process of Pt/C formation in N2 showed very good control over Pt particle size whereas the Pt loading is significantly low. When the process of Pt/C formation is carried out in the presence of O₂, the Pt loading is increased up to 36 wt%. However, the particle size of Pt increases due to agglomeration at low solution pH. As a modification to the polyol process, the reduction of Pt metal ions at elevated temperature with N₂ purging followed by the further reduction at room temperature with air showed the best results with almost 40 wt% loading and a small particle size of 2.8 nm.

Acknowledgement

This work is supported by Hyundai Motors and the Ministry of Commerce, Industry and Energy.

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