

폴리올 프로세스를 통한 연료전지용 백금 촉매 제조

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Investigation of carbon supported Pt nano catalyst preparation by the polyol process for fuel cell applications

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Key words : Polyol process, ethylene glycol, zeta potential, PEM fuel cells

Abstract : Parametric investigation of the polyol process for the preparation of carbon supported Pt nano particles 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 39.5wt% 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.

1. Introduction

There is tremendous interest in the preparation of carbon supported 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].

In the present work, a modified polyol process is utilized for nano sized 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

A measured amount of PtCl₄ and NaOH were dissolved in 25ml 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 40wt% of Pt/C. The resulting suspension was stirred for 1hr at room temperature followed by heating

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under reflux at 160°C for 3 hrs. The solution was allowed to cool down to room temperature and left for 12 hrs 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 1h 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.

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. [19].

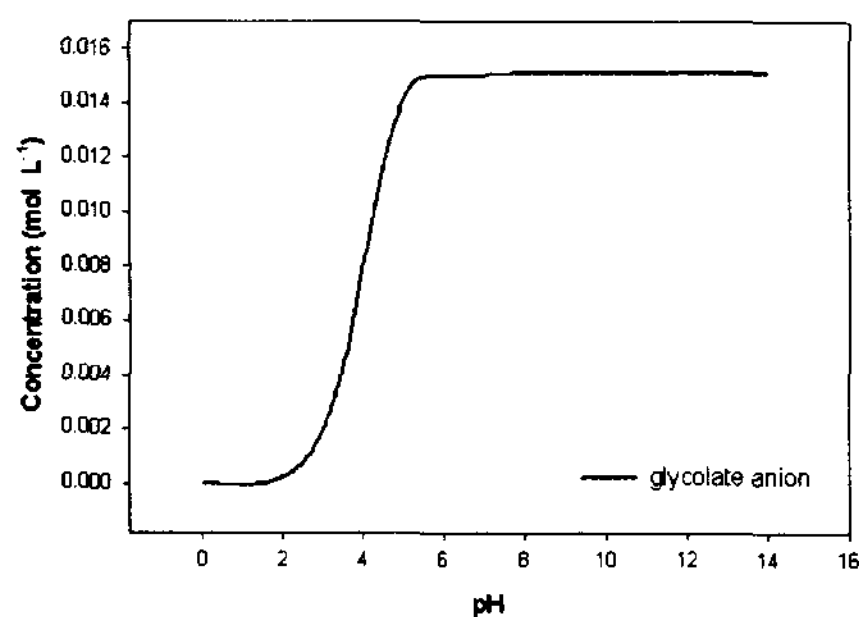
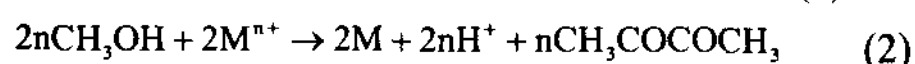


Fig. 1 Dependence of glycolate anion concentration as a function of pH

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 nano catalysts [18], 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

$1.48 \times 10^{-4} \text{ molL}^{-1}$ at 25°C. This implies that glycolic acid is present in its deprotonated form as the glycolate anion in alkaline solutions. Glycolate ion is considered to act as a stabilizer by forming chelate-type complexes via its

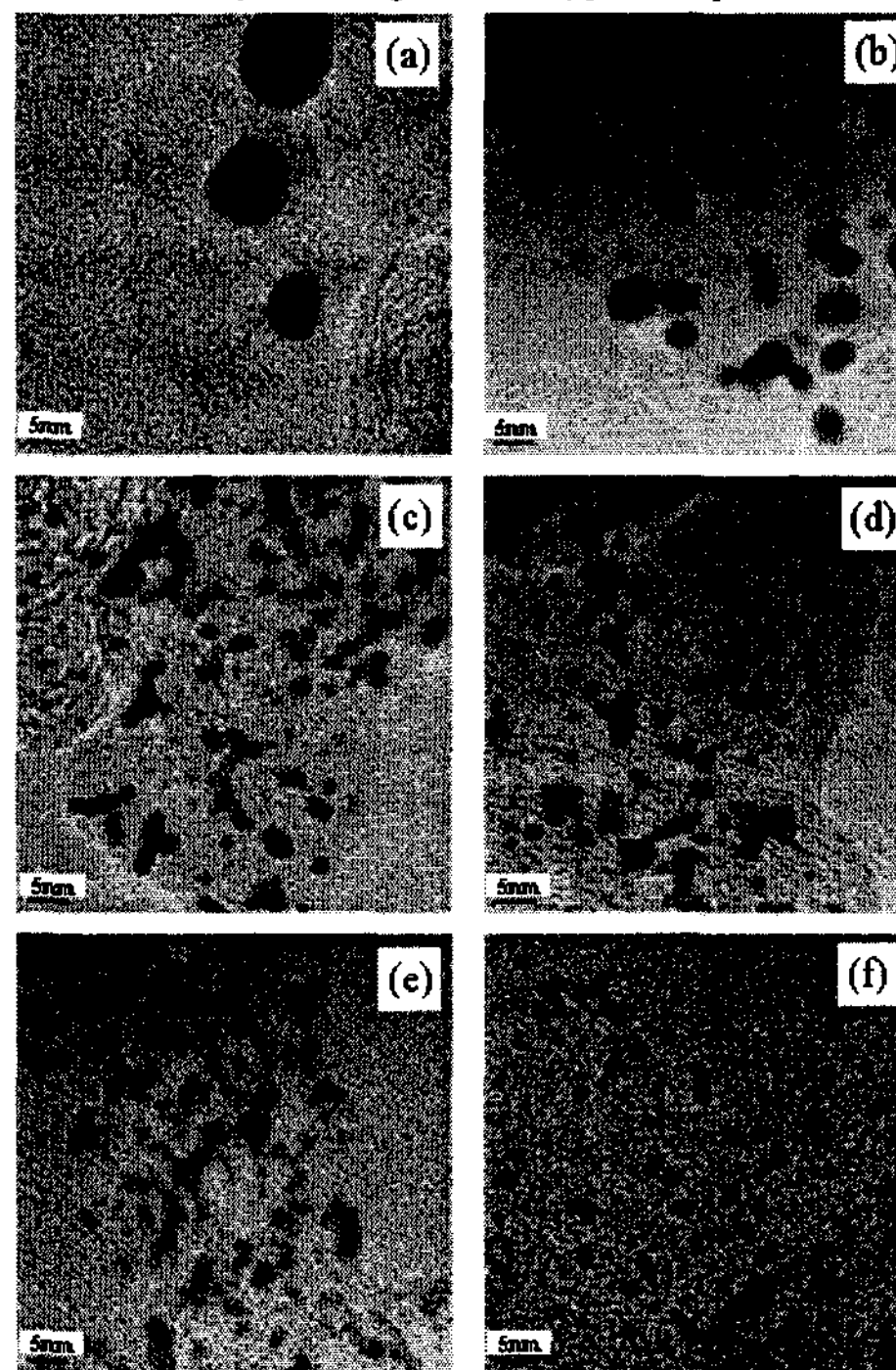


Fig. 2 HR-TEM images of Pt particles on Ketjen black 300J prepared at different NaOH concentrations

carboxyl groups [18]. 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 to 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. 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 significant above 0.1M 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.

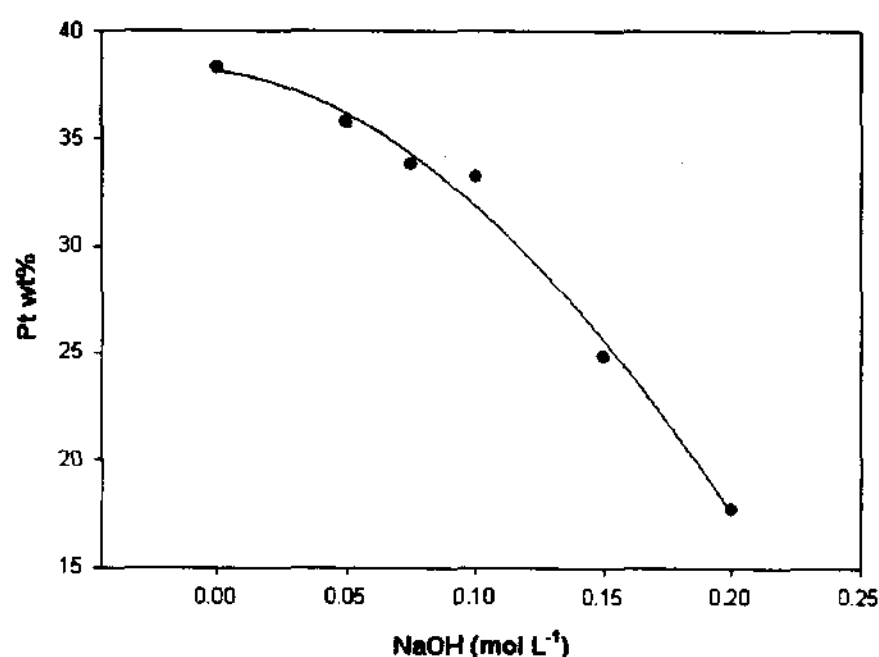


Fig. 3 The variation of Pt wt% deposited on carbon black as a function of NaOH concentration

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. 3. 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

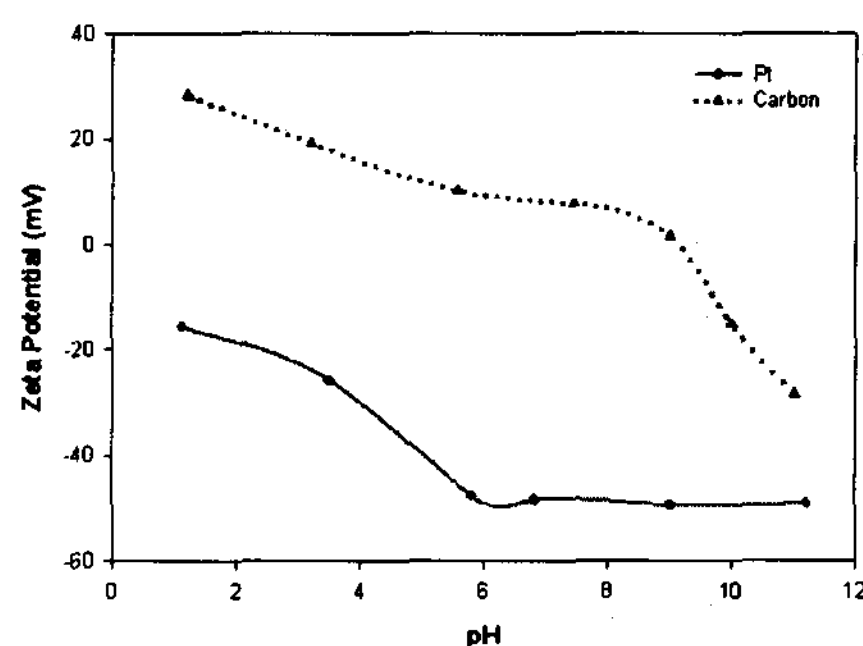


Fig. 4 Effect of changing solution pH on the zeta potential of Pt particles and carbon black

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. 4. 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 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. 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 mainly

by the electrostatic repulsive force between carbons and Pt particles.

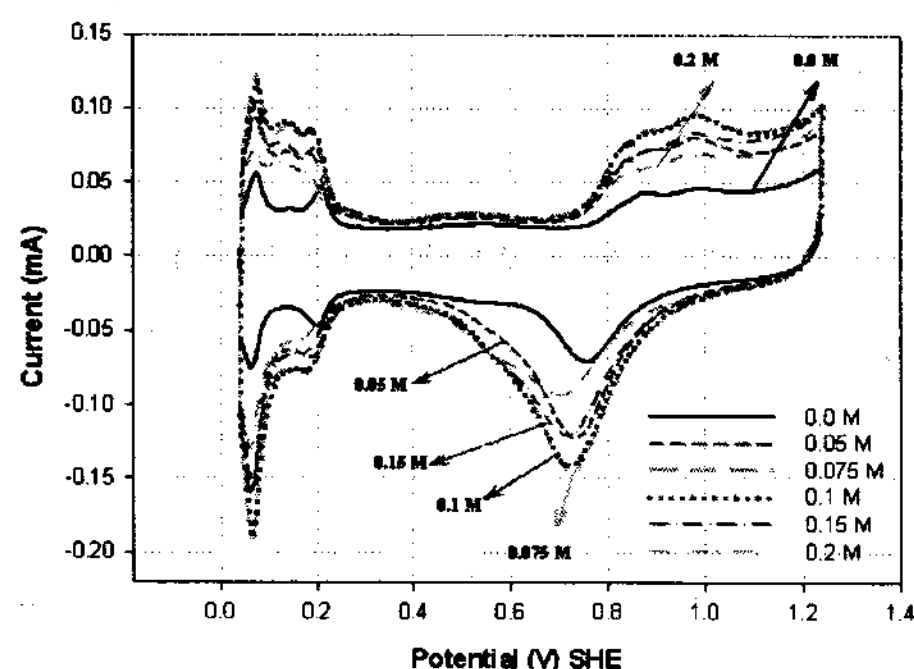


Fig. 5 Cyclic voltammograms of the Pt/C catalysts prepared at different NaOH concentrations in 0.5 M H_2SO_4 solution at $5mVs^{-1}$.

Fig. 5 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 H_2SO_4 as an electrolytic solution at a scan rate of $5 mVs^{-1}$ with N_2 purging. The effective surface area of the carbon supported Pt nano particles 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 $210 \mu C cm^{-2}$. 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. 6. 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.

4. Conclusion

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 nano dimension 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 N_2 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 O_2 , 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 N_2 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.

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