

Polyol process를 통한 고비율 백금 담지 촉매 합성

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Novel route of enhancing the metal loading in highly active Pt/C electro-catalyst by polyol process

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Abstract : A modified polyol process is developed to enhance Pt loading during the preparation of Pt/C catalysts. With the help of the zeta potential, the effect of pH on the electrostatic forces between the support and the Pt colloid is investigated. It is shown experimentally that the surface charge on the carbon support becomes more electropositive when the solution pH is changed from alkaline to acidic. However, this change does not affect the electronegative surface charge of Pt colloids already attained and stabilized by glycolate anions. This new behavior caused by the change in the solution pH accounts for the enhanced yield of the process and does not affect the Pt particle size. All our experimental results reveal that this simple modification is a cost effective method for the synthesis of highly Pt loaded Pt/C catalysts for fuel cells.

1. Introduction

Carbon supported platinum (Pt/C) catalysts have been the most widely used in fuel cells due to their high activity toward the oxygen reduction reaction at low temperature [1-4]. It is well known that the performance of a fuel cell depends strongly on the apparent exchange current density of the Pt/C electrode which is influenced by the roughness factor [5]. This is based on the assumption that the nature of the oxygen reduction reaction on Pt does not change. Since the roughness factor is the ratio between the actual active surface area of the catalyst and the geometrical electrode area, it depends directly on the total surface area of Pt and hence on the particle size and amount of Pt contained in the electrode. The total Pt content in the electrode increases as the thickness of the electrocatalyst layer increases. However, when the catalyst layer is thicker than 10 μm this results in low catalyst utilization due to the transport limitations of dissolved oxygen and protons in the ionomer [6]. Therefore, extensive research has been carried out to achieve a uniform distribution of nano-sized particles as well as high loading of Pt over carbon supports [7-9].

Previous studies have revealed the difficulty of increasing the metal loading without a significant increase in the particle size [10,11]. In this respect, the polyol process has received high attention because it provides a satisfactory control of Pt particle size and distribution without using any additional stabilizer [12-14]. In the polyol process using ethylene glycol, metal ions are reduced to form a metal colloid by receiving electrons from the oxidation of ethylene glycol to glycolic acid, which is present in its deprotonated form as glycolate anions in alkaline solution. The glycolate anions adsorbed on the surface of the metal act as a stabilizer giving rise to an electrostatic repulsive force between metal particles. Consequently, a strong relationship exists between the concentration of glycolate anion and the particle size of the metal in solution. The glycolate anion concentration increases with increasing pH and a major change is evident in the pH range between 2 and 6. Therefore, it is more favorable to

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perform the polyol process in an alkaline solution in order to decrease the Pt particle size [15,16]. catalyst was used as the working electrode while platinum wire and standard Hg/HgSO₄ electrode were used as counter and reference electrodes, respectively. The size and distribution of the Pt particles prepared by the polyol process was determined by high resolution transmission electron microscopy (HR-TEM, JEM- 30100 model) and thermo gravimetric analysis (TGA) was carried out to estimate the Pt loading of the carbon support. The surface charge of the carbon support and Pt colloid particles was measured as a function of pH using a zeta potential (Malvern Instruments ZEN 3600).

3. Results and Discussion

Pt/C catalysts with different Pt ratios were synthesized using the conventional polyol process by using the calculated amount of Pt salts and carbon supports in the solution. The resulting Pt content in the Pt/C catalyst was evaluated using TGA analysis and the results are given in Fig. 1.

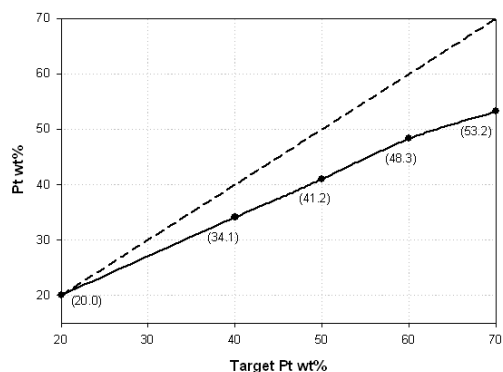


Fig. 1 The composition analysis of Pt in the Pt/C catalysts using TGA.

If all of the Pt salt was reduced and loaded on to the carbon support with no loss, the measured Pt wt.% should be the same as the target wt.%. However, the measured Pt wt.% is below the diagonal line of the graph indicating that the Pt particles are not completely loaded on to the carbon support. The discrepancy between the measured and the targeted Pt ratio increases with increase of the target Pt wt.%. The Pt particles which are not loaded on to carbons remain in the solution and must be considered to be wasted. Since Pt is a precious metal, the production yield of the process is really a catalyst cost benchmark. According to our previous study, the reduction of yield in the polyol process could be explained by way of the dominant electrostatic repulsive force between the Pt particles and carbon support [16]. The zeta potential measurement showed that both the carbon support and Pt colloids in alkaline solution

possessed a strong negative surface charge resulting in an electrostatic repulsive force.

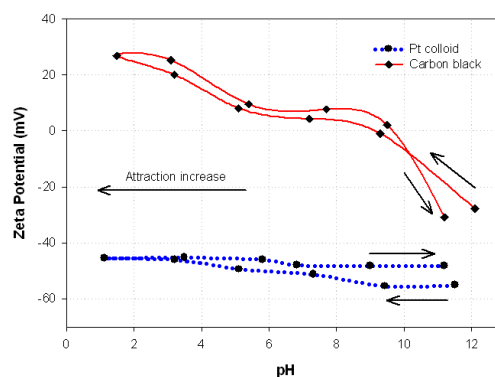


Fig. 2 The change in zeta potential of the Pt colloid and the carbon support on changing the pH from alkaline to acid and vice versa.

The surface charge in the polyol process originates from the adsorption of glycolate anion and hydroxyl ion. It was reported that the concentration of both ions depends on the pH of the solution. However, it was expected that the adsorption strength of ions to substrates might be different. In order to prove this assumption, the surface charge of the carbon and the Pt colloid was measured individually as a function of pH in the polyol process.

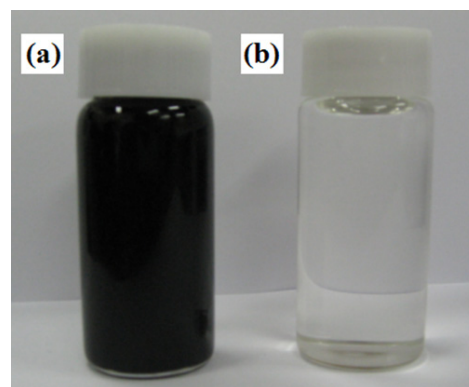


Fig.3 Filtered solution of the polyol process (a) without the pH adjustment step, (b) with the pH adjustment step.

Initially, the polyol reaction was performed at the pH of 12. Once the reaction was complete, the pH of the solution was varied by using H₂SO₄ and NaOH. As presented in Fig 2, the zeta potential of the carbon moves from a negative to a positive value when changing the pH from 12 to 1.5. As the pH reverses to 12, the zeta potential changes to a negative value again. However, in contrast to carbon, no significant change in the zeta potential is observed when the pH of the solution changes from alkaline to acidic and vice versa, which implies that the glycolate anions are adsorbed on the

surface of Pt colloids more strongly than that of carbons and are not replaced by other ions. This result provides an important clue to solving the observed problem in the polyol process. After the polyol reaction is carried out above a pH of 6 where the concentration of glycolate anion is at saturation, the pH of the solution is reduced to around 3 to provide the carbon support with a positive surface charge during this step the negative surface charge of the already stabilized Pt colloid remains constant. Subsequently, it is believed that the present strategy helps to increase the electrostatic attraction between the carbon support and the Pt colloid resulting in high Pt loading without also increasing the Pt particle size.

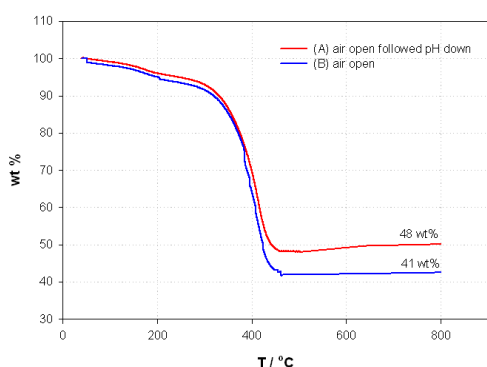


Fig. 4 TGA analysis of the Pt/C catalysts prepared by the polyol process with and without the pH adjustment step. The target is 50 wt.% of Pt.

The scheme described above was experimentally verified simply by a comparison of the filtered solution from the polyol process with and without the pH adjustment step. From Fig. 3, the color of the filtered solution changes from black to transparent after the pH adjustment step. The clear solution is the direct evidence that no suspended Pt colloidal particles remain in the filtered solution therefore increasing the yield of the polyol process. The effect of the pH adjustment step on the increase in the yield of the process is further confirmed by estimating the loaded Pt content using TGA analysis. As seen in Fig. 4, the target 50 wt.% of Pt is almost achieved by the new process. However, the Pt/C sample without the pH adjustment step shows just 41 wt.%, which is much lower than the target wt.%.

The variation of particle size and dispersion of Pt in Pt/C with respect to the use of the pH adjustment step were examined by HR-TEM. As seen in Fig. 5, a surprising result is found in that the particle size of Pt appears to be almost constant after using the pH adjustment step. This is explained by the fact that the surface charge of Pt is not affected by the pH adjustment step as illustrated by the zeta potential experiment. As a

result the electrostatic repulsive force existing between Pt particles prevents any aggregation.

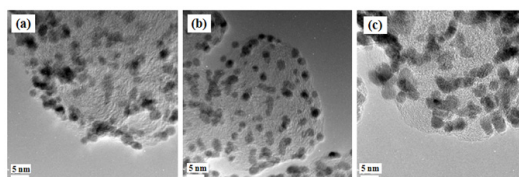


Fig. 5 HR-TEM micrographs of Pt/C prepared by the polyol process (a) without the pH adjustment step, (b) with the pH adjustment step and (c) the commercial Pt/C (50 wt.% Pt from Johnson Matthey).

Fig. 6 shows cyclic voltammograms of the Pt/C catalysts (target: 50 wt.% of Pt) prepared by the polyol process with and without the pH adjustment step. The commercial 50 wt.% sample of Pt/C was also tested for comparison.

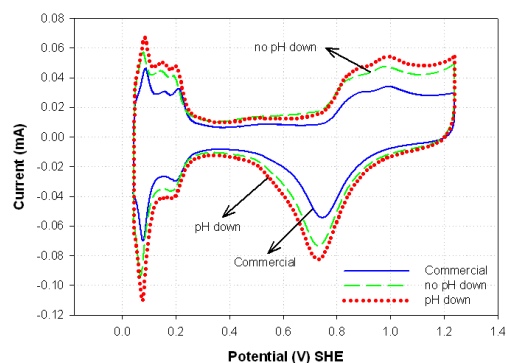


Fig. 6 Effect of the pH adjustment step on the cyclic voltammograms of Pt/C prepared by the polyol process (and the commercial Pt/C for comparison) in 0.5 M H₂SO₄ solution at 5 mV s⁻¹.

The CVs were performed in 0.5 M H₂SO₄ saturated with N₂ at a scan rate of 5 mV s⁻¹. The effective surface area of Pt was calculated from the area of the hydrogen desorption peak 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 a conversion factor of 210 μC cm⁻² [17].

targeted Pt loading (wt.%)	Pt wt.% from TGA		Active surface area (m ² g ⁻¹)		Particle size from HR-TEM (nm)	
	pH change	without pH change	pH change	without pH change	pH change	without pH change
40	38.2	34.1	64.7	64.6	2.1	2.2
50	47.9	41.2	58.0	57.9	2.6	2.6
60	56.8	48.3	54.1	53.1	3.2	3.1
70	64.8	53.2	49.3	48.7	3.4	3.3

Table 1. The effect of the pH adjustment step on the loading, specific active surface area and the particle size of the Pt/C catalyst prepared by the polyol process.

As seen in Fig. 6, the CV of Pt/C with the pH adjustment step shows an increase in the area of the hydrogen desorption peak compared with the other samples. This result can be attributed to the increase in the wt.% of Pt in Pt/C together with the decrease in the particle size of Pt as confirmed from the TGA and HR-TEM analyses. The effect of pH adjustment on the Pt wt.%, the specific active surface area and the particle size of Pt for different targeted wt.% of Pt/C are summarized in Table 1. It is clear from this data that the pH adjustment step does affect the yield of the process. By introducing the pH adjustment step to the polyol process, the Pt wt.% approaches the target value and furthermore, the particle size of Pt appears to remain unchanged. Therefore it can be concluded that the pH adjustment is a very effective way of increasing the yield of the polyol process without sacrificing the particle size of Pt.

4. Conclusions

The yield of polyol process is enhanced without affecting the particle size of Pt by introducing the pH adjustment step. When the pH adjustment step is added at the end of a conventional polyol process to synthesize 50 wt.% of Pt/C, approximately 96% of the Pt added initially to the solution is used to form the Pt/C catalysts this yield is higher by 14% than in the absence of this step. This result is attributed to the change of electrostatic forces. According to the zeta potential measurement, the strong adsorption of glycolate anion on the surface of Pt colloids generates a negative surface charge and ensures that the electrostatic repulsive force generated along with the change of pH prevents the Pt colloids from aggregating. On the other hand, the surface charge of the carbon support is dependent on the pH of the solution. Therefore, the Pt colloids, already negatively stabilized, experience increased electrostatic attractive force due to the highly electropositive carbon surface in acidic solutions. This results in a highly loaded Pt/C catalyst with a minimal loss of Pt.

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References

1. Z. Tang, D. Geng, G. Lu, 2005, *J. Colloid and Interface Science*, 287, 159-166.
2. H. Kim, B.N. Popov, 2004, *Electrochim. Solid-State Lett.*, 7, A71-A74.
3. S. Hirano, J. Kim, S. Srinivasan, 1997, *Electrochim. Acta*, 42, 1587-1593.
4. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, M. A. El Sayed, 1996, *Science*, 272, 1924-1925.
5. X. Li, *Principles of Fuel Cells*, New York, 2006, pp 152-155, Taylor & Francis Group
6. D. M. Bernardi, M. W. Berbrugge, 1991, *AIChE J.*, 37, 1151-1163.
7. M.S. Wilsn, S. Gottesfeld, 1992, *J. Appl. Electrochem.*, 1, 1-7.
8. Z. Liu, L M Gan, L. Hong, W. Chen, J. Y. Lee, 2005, *J Power Sources*, 139, 73-78.
9. X. Yan, H. Liu, K. Y. Liew, 2001, *J Mater. Chem.*, 11, 3387-3391.
10. A Gamez, D. Richard, P. Gallezot, F. Gloaguen, R. Faure, R. Durand, 1996, *Electrochim. Acta*, 41, 307-314.
11. M. Watanabe, K. Sakairi, US Patent 5,728,485 (1998).
12. M. Watanabe, M. Uchida, S. Motoo, 1987, *J. Electroanal. Chem.*, 229, 395-406.
13. T. Masaharu, H. Masayuki, N. Yuki, 2004, *Mater. Lett.*, 58, 2326-2330.
14. Y. J. Zhu, X. L. Hu, 2004, *Mater. Lett.*, 58, 1234-1236.
15. C. Bock, C. Paquet, M. Couillard, G. A. Botton, B. R. MacDougall, 2004, *J. Am. Chem. Soc.*, 126, 8028-8037.
16. H.S Oh, J. G Oh, Y. G. Hong, H. Kim, 2007, *Electrochim. Acta*, 52, 7278-7285.
17. A. J. Bard, *Electroanalytical Chemistry*, Vol. 9, Marcel Dekker, New York and Basel, 1976, pp 56-57.