



## Short communication

## Modification of polyol process for synthesis of highly platinum loaded platinum–carbon catalysts for fuel cells

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## ABSTRACT

A modified polyol process is developed to enhance the Pt loading during the preparation of carbon-supported platinum (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. This change does not, however, affect the electronegative surface charge of Pt colloids already attained and stabilized by glycolate anions. This new behaviour caused by the change in solution pH accounts for the enhanced yield of the process and does not affect the Pt particle size. All the 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.

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## 1. Introduction

Carbon-supported platinum (Pt/C) catalysts have been the most widely used in fuel cells due to their high activity towards 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 that 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. When, however, the catalyst layer is thicker than 10  $\mu\text{m}$  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 [10,11] have revealed the difficulty of increasing the metal loading without a significant increase in the particle size. In this respect, the polyol process has received high atten-

tion 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 and give rise to an electrostatic repulsive force between the 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 favourable to perform the polyol process in an alkaline solution in order to decrease the Pt particle size [15,16]. It has been reported, however, that the Pt content of carbon supports decreases significantly with increasing alkalinity of the polyol solution [16]. The unsupported Pt particles remain in solution and end up as a loss of Pt during synthesis. Since Pt is an expensive material and a major contributor to the cost of a fuel cell, it is a critical factor in the selection of a Pt/C preparation technique.

In this study, the conventional polyol process is modified by simply adding a pH adjustment step in order to increase the Pt content on the carbon support without any noticeable increase in the particle size. It is accomplished by increasing the electrostatic attractive force between Pt colloids and carbons while maintaining the electrostatic repulsive force between Pt particles. This can be

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satisfactorily explained using a zeta potential measurement on the Pt colloids and carbon supports as a function of pH.

## 2. Experimental

### 2.1. Preparation of Pt/C catalyst

A measured amount of  $\text{PtCl}_4$  was dissolved in 25 ml of ethylene glycol under vigorous stirring for 30 min. 0.1 M NaOH was introduced to the solution to adjust the pH. Since it is so important to the polyol process, the pH of the solution was precisely controlled and recorded at every step. The calculated amount of carbon black (Ketjen black 300J) as support was added to the solution to produce 20, 40, 50, 60 and 70 wt.% Pt loading on the carbon support. The resulting suspension was stirred for 1 h at room temperature followed by reflux at  $160^\circ\text{C}$  for 3 h. The solution was allowed to cool down to room temperature and left for 12 h with continuous stirring. 0.1 M  $\text{H}_2\text{SO}_4$  was then added to the cooled mixture and the solution pH was adjusted to 3. The mixture was kept stirred for 24 h. The Pt/C powder in the solution was filtered and thoroughly washed with water. The resulting carbon-supported Pt catalyst was dried in air for 1 h at  $160^\circ\text{C}$  and a mortar was used to homogeneously grind the material to form a fine powder.

### 2.2. Characterization

Cyclic voltammetry was used to determine the effective active surface area of the Pt/C catalyst and to estimate the Pt particle size. The experiment was performed in 0.5 M  $\text{H}_2\text{SO}_4$  saturated with nitrogen and contained within a conventional three-electrode cell. A glassy carbon electrode with a thin film of prepared Pt/C catalyst served as the working electrode while platinum wire and a standard  $\text{Hg}|\text{HgSO}_4$  electrode were used as the counter and the reference electrode, respectively. The size and distribution of the Pt particles prepared by the polyol process was determined by means of 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 via the conventional polyol process by using the calculated amounts of Pt salts and carbon supports in the solution. The resulting Pt content in the Pt/C catalyst was evaluated by TGA analysis and the results are given in Fig. 1. 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.%. In fact, the measured Pt wt.% is below the diagonal line of the graph and this indicates 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 in 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 benchmark for catalyst cost.

According to our previous study [16], the reduction in yield from the polyol process could be explained in terms of the dominant electrostatic repulsive force between the Pt particles and carbon support [16]. Zeta potential measurements showed that both the carbon support and Pt colloids in alkaline solution possessed a strong negative surface charge which resulted in an electrostatic

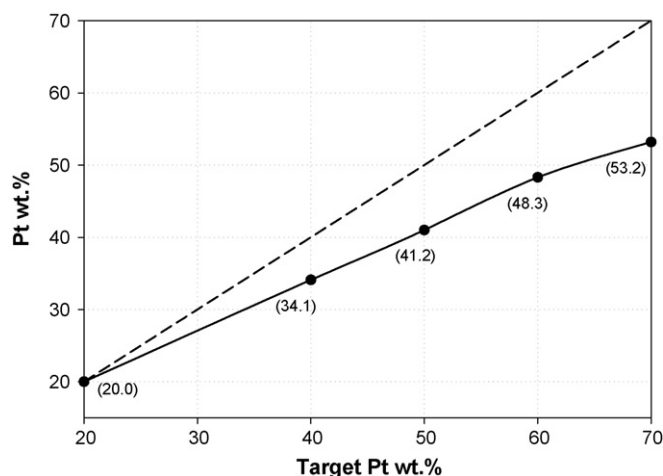


Fig. 1. Composition analysis of Pt in Pt/C catalysts using TGA.

repulsive force. The surface charge in the polyol process originates from adsorption of glycolate anion and hydroxyl ion. It was reported that the concentration of both ions depends on the pH of the solution. It was expected, however, 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 were measured individually as a function of pH in the polyol process. Initially, the polyol reaction was performed at a pH of 12. Once the reaction was complete, the pH of the solution was varied by using  $\text{H}_2\text{SO}_4$  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. In contrast to carbon, however, 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 surface with a positive surface charge; during this step the negative surface charge of the already stabilized Pt colloid remains constant. Subsequently, it is believed

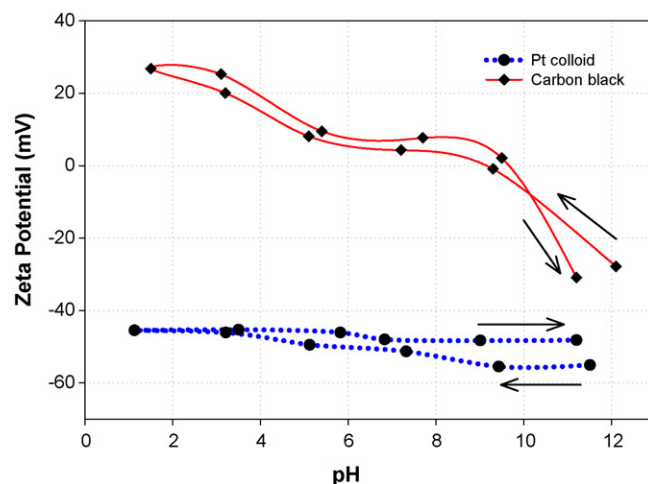
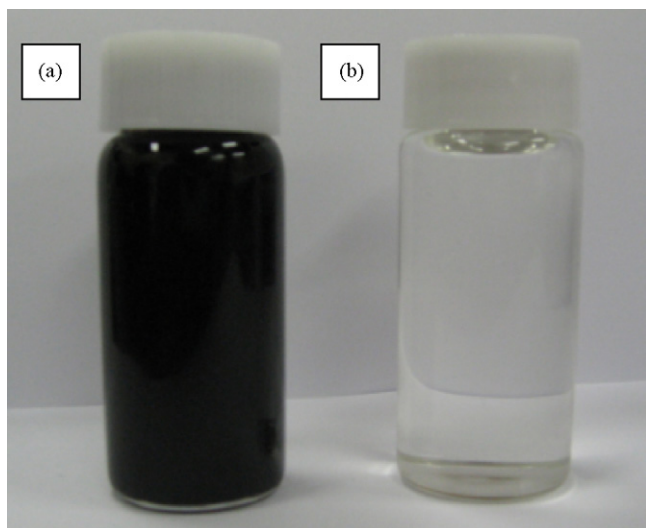
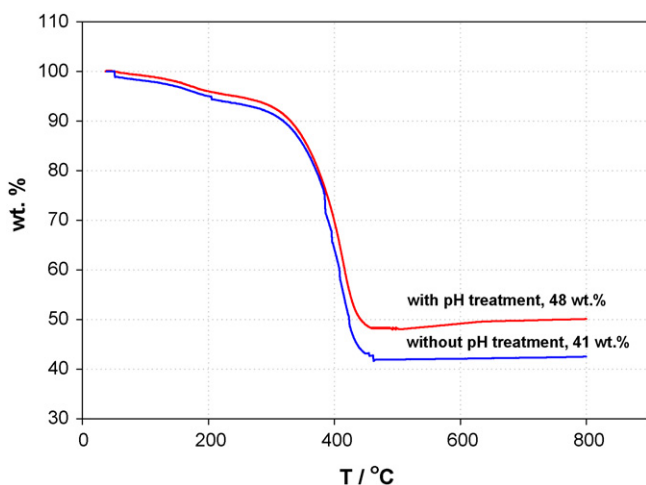


Fig. 2. Change in zeta potential of Pt colloid and carbon support on changing the pH from alkaline to acid, and vice versa.

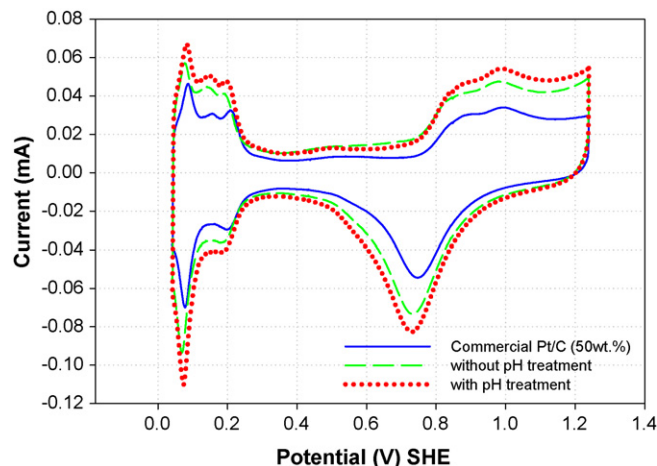


**Fig. 3.** Filtered solution of polyol process (a) without pH adjustment step and (b) with pH adjustment step.



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

that the present strategy helps to increase the electrostatic attraction between the carbon support and the Pt colloid and there by results in high Pt loading without also increasing the Pt particle size.



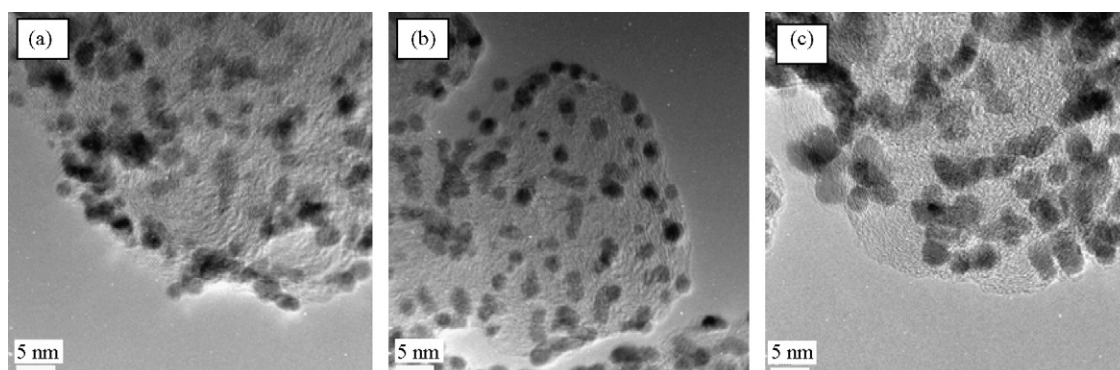
**Fig. 6.** Effect of pH adjustment step on cyclic voltammograms of Pt/C prepared by polyol process (and commercial Pt/C for comparison) in 0.5M  $\text{H}_2\text{SO}_4$  solution at  $5 \text{ mV s}^{-1}$ .

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 colour of the filtered solution changes from black to transparent after the pH adjustment step. The clear solution is direct evidence that no suspended Pt colloidal particles remain in the filtered solution and therefore the yield of the polyol process is increased.

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. By contrast, 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 was 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. Consequently, the electrostatic repulsive force existing between Pt particles prevents any aggregation.

Cyclic voltammograms (CVs) of the Pt/C catalysts (target: 50 wt.% of Pt) prepared by the polyol process with and without the pH adjustment step are presented in Fig. 6. A commercial 50 wt.% sample of Pt/C was also tested for comparison. The CVs were performed in 0.5 M  $\text{H}_2\text{SO}_4$  saturated with  $\text{N}_2$  at a scan rate of  $5 \text{ mV s}^{-1}$ . The effective surface area of Pt was calculated from the area of the



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

**Table 1**

Effect of pH adjustment step on loading, specific active surface area and particle size of Pt/C catalysts prepared by the polyol process

Targeted Pt loading (wt.%)	Pt wt.% from TGA		Active surface area (m <sup>2</sup> g <sup>-1</sup> )		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

hydrogen desorption peak between 0.03 and 0.3 V (SHE) after subtracting the contribution from double layer charging. This area is converted into the effective active surface area of Pt using a conversion factor of 210  $\mu\text{C cm}^{-2}$  [17]. 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 is summarized in Table 1. It is clear from this data that the pH adjustment step does affect the yield of the process. By introducing this 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 pH adjustment is a very effective means of increasing the yield of the polyol process without sacrificing the particle size of Pt.

#### 4. Conclusions

The yield of the polyol process is enhanced without affecting the particle size of Pt by introducing a pH adjustment step. When the 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. The yield from the pH adjustment step is 14% higher than that in the absence of the step. This result is attributed to a change of electrostatic forces. According to zeta potential measurements, 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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