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Polyol Precess를 통한 PEM Fuel Cell용 Pt/C 촉매 제조

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Preparation of Pt/C catalyst for PEM fuel cells using polyol process.

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Key words : Pt nanoparticles, catalyst, Fuel cell, Polyol pross

Abstract : Carbon-supported Platinum (Pt) is the potential electro-catalyst material for anodic and cathodic reactions in fuel cell. Catalytic activity of the metal strongly depends on the particle shape, sizeand distribution of the metal in the porous supportive network. Conventional preparation techniques based on wet impregnation and chemical reduction of the metal precursors often do not provide adequate control of particle size and shape. We have proposed a novel route for preparingnano sized Pt colloidal particles in solution by oxidation of ethylene glycol. These Pt nano particles were deposited on large surface area carbon support. The process of nano Pt colloid formation involves the oxidation of solvent ethylene glycol to mainly glycolic acid and the presence of its anion glycolate depends on the solution pH. In the process of colloidal Pt formation glycolate actsas stabilizer for the Pt colloidal particle and prevents the agglomeration of colloidal Pt particles. These mono disperse Pt particles in carbon support are found uniformly distributed in nearly spherical shape and the size distribution was narrow for both supported and unsupported metals. The average diameter of the Pt nano particle was controlled in the range of 2 to 3 nm by optimizing reaction parameters. Transmission electron microscopy, CV and RRDE experiments were used to compliment the results.

1. Introduction

Carbon supported Platinum nanoparticles as cathode catalysts have attracted wide attention as a candidate to achieve high performance, to increase in power density, and to reduce a component cost of PEMFCs [1]. Metal nanoparticles with carbon support has come up as an excellent catalysts for direct methanol fuel cell (DMFC) and proton exchange membrane fuel cell (PEMFC) device. The synthesis of nanometer-sized noble metal particles with uniform distribution in catalyst for fuel cell is important in catalytic process due to their high surface area per unit volume [2]. There are continuing efforts to develop alternative synthetic methods based on microemulsion, sonochemistry, and microwave irradiation and so on [3].

The size and distribution of Pt nano particles in the carbon support is the most critical parameter for catalysis. Synthetic procedure of nanoparticles has been attracting high interest for a long time due to Considerable potential applications of metal particles in nano size. Researchers have been paying lot of attention to the size and shape of the nano particle by investigating newer synthetic procedures. Among the available techniques Conventional preparation methods based on wet impregnation and chemical reduction of the metal precursors often do not provide adequate control of particle shape and size.

Through this work we report a novel method of preparing colloidal solution of Pt nano particles synthesized in ethylene glycol [4]. The effect of pH in the dispersity of the colloidal solution and the dependence of particle size on the concentration of sodium hydroxide were studied with high resolution

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transmission electron microscopy (HRTEM).

2. Experimental

The synthesis of the Pt colloids was carried out in ethylene glycol solution by . The solution of $PtCl_4$ and NaOH in ethylene glycol was stirred for 30 min in air at room temperature followed by heating under reflux at 160°C for 3h. The color of the solution was found to change from a clear light yellow to a transparent black-brown after reflux. The change in colour from light yellow to dark brown is the indication of colloidal Pt formation in the solution. The solution was allowed to cool down to room temperature and after that appropriate aliquots of the colloidal solutions were mixed with Vulcan XC-72R. This resulted in the deposition of the Pt colloids on the carbon surface. The carbon-supported Pt catalysts were then filtrated and extensively washed with water. The carbon-supported Pt catalysts were dried in air at 160°C for 1 h. A mortar was used to homogeneously ground the carbon-supported catalyst powders. Electrochemical experiments were carried out using cyclic voltammetry (CV), and rotating ring disk electrolyte (RRDE). HRTEM was used for analyzing the particle size.

3. Results and discussion

Considering the importance of particle size and the distribution for a good catalyst material we have used High Resolution TEM to analyze the catalyst prepared in ethylene glycole and compared that with the commercially available. Figs 1 (a) and (b) have been depicted to have a comparison between a commercially available Pt/C catalyst and the catalyst prepared by the method in discussion.

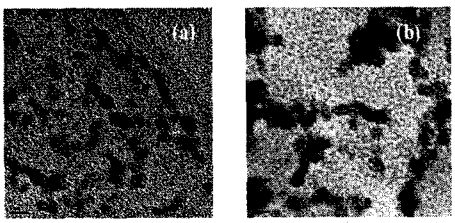


Fig 1. HRTEM images of (a) the prepared Pt deposited on Vulcan XC72R by polyol process (NaOH 0.1M, gas condition : air open) and (b) the commercial 40wt% Pt/C. The bar indicate a 5nm scale. The magnifications were used to obtain the HRTEM images: X400000

The HRTEM image in Fig.1 (a) show uniformly distributed black spots with a particle size of 2~3nm. These black spot shows that the Pt nano particle of 2-3 nanometer is nicely confined with the Vulcan XC-72R particle. Furthermore, the Pt nanoparticles were not aggregated, which implied that the Pt nanoparticles were well-dispersed in the solution. Whereas the distribution and size of Pt nano particles for commercial Pt/C catalyst in Fig.1 (b) showed that the black spots due to Pt particles were of 3-5nm observed on the carbon support and the distribution is comparatively poor and the Pt nano clusters due to agglomeration is also observed. In summary of the HRTEM results for the two catalysts it was concluded that Pt nanoparticles by ethylene glycol are smaller than Pt that of commercial Pt/C. this supports the novelty of the proposed process of Pt particle formation by ethylene glycol

Electrochemical characterization of ethylene glycol synthesized Pt/C catalyst electrode was carried out using Pine Electrochemical instrument. Conventional three compartment electrochemical cell, in which reference counter and working electrodes were separated was used for CV and RRDE experiments. Hg/HgSO4 electrode was used for the reference potential measurement and a platinum sheet was used for the counter electrode. The voltagram recorded for Pt/C by ethylene glycol catalyst is shown in Fig 2.

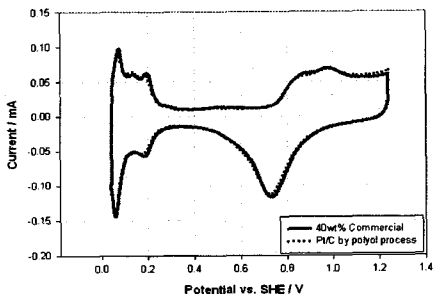


Fig 2. Cyclic voltammetry curves graph of the prepared Pt deposited on Vulcan XC72R by polyol process (NaOH 0.1M, gas condition : air open) Cyclic voltammograms recorded at $5mVs^{-1}$ in 0.5 M H_2SO_4 solutions.

Nitrogen was continuously bubbled through the electrolyte. Cyclicvoltagram recorded in a range of -0.6 to 0.4 V (Hg/HgSO4) at 5mV/s show typical character of Pt/C catalyst. Results of commercial

and ethylene glycol synthesized electrode are summarized in table (1).

	Pt wt%	H_2 adsorption area (10^{-3} C)	Spt (m^2/g)
Prepared Pt/C by Polyol process	38.7	2.15	88.9
Commercial 40wt% Pt/C	29.5	2.18	68.5

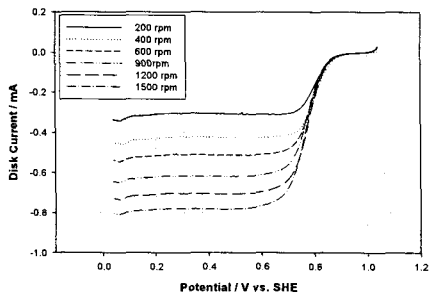
Table 1. Compare Pt/C particle size by cyclic voltammetry curves

The particle diameter of synthesized Pt/C and commercial 40wt% Pt/C catalysts determined by CV as shown in Table 1. shows that the ethylene glycol synthesized Pt nanoparticles are smaller than Pt nanoparticles in commercial available 40wt% Pt/C.

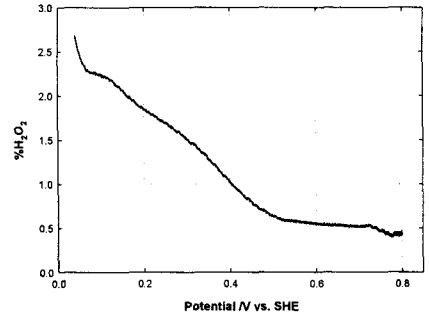
The rotating ring electrode data at various rotating rates for ethylene glycol synthesized Pt/C catalyst is shown in Fig.3 (a). The onset potentials shown here are high compared to commercial Pt/C. The high onset potential showed that the Pt/C prepared by ethylene glycol has uniform distribution of Pt particles and has better catalytic action. The rate of hydrogen peroxide formation is shown in Fig3 (b). The molar fraction of H_2O_2, can be calculated from disk and ring current, ID and IR, respectively, based on Equation below.

$$n = 4I_D/(I_D + (I_R/N))$$

$$\%H_2O_2 = 100(4-n)/2 = 100\frac{2\,I_R/N}{I_D + I_R/N}$$



(a)



(b)

Fig 3. (a) Disk current of the prepared Pt deposited on Vulcan XC72R by polyol process (NaOH 0.1M, gas condition : air open) (b) Hydrogen peroxide rate of the prepared Pt deposited on Vulcan XC72R by polyol process (NaOH 0.1M, gas condition : air open)

The rate of Hydrogen peroxide formation for Pt/C by prepared ethylene glycol is shown in Fig.3 (b). This is less than 3.0% and is comparable to commercial Pt/C catalyst.

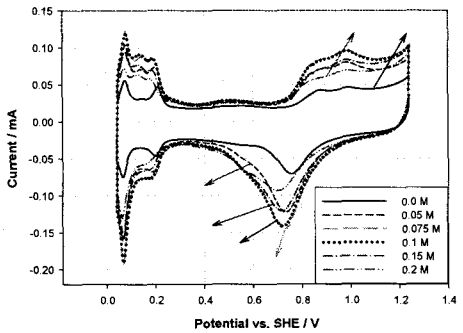


Fig 4. Cyclic voltammograms of the Pt/C catalysts prepared at different NaOH concentration. Cyclic voltammograms recorded at 5mVs-1 in 0.5 M H2SO4 solutions.

The voltagram recorded for Pt/C catalysts by polyol process at different pH is shown in Fig 4.

The resulting particle size distributions obtained from HRTEM images for Pt colloids synthesized using the different NaOH concentrations are shown in Fig 5. All HRTEM images were obtained for Ketjen Black 300J supported Pt catalysts. Particle size of Pt loading on carbon depends on the pH of synthesis solution in the

polyol process. With increasing pH of solution, the particle size of Pt decreased from 8.5nm to 2.2nm and the amount of Pt loading on carbon was reduced from 38.3 to 17.7wt%. The pH of solution is adjusted by the different amount of NaOH.

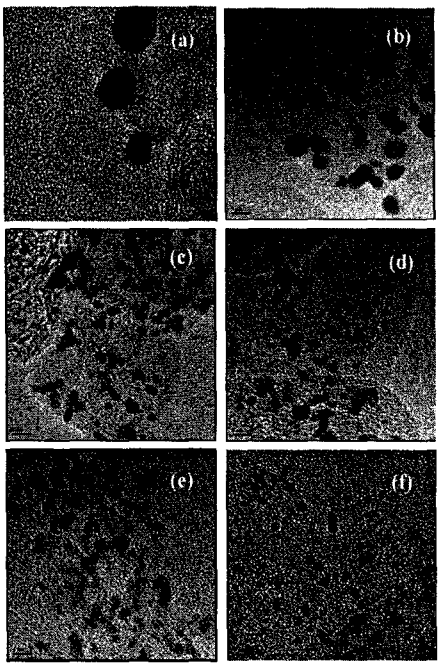


Fig 5. HRTEM images of Pt catalysts deposited on Ketjen Black 300J. Pt/C catalysts prepared at different NaOH concentration. (a) 0.0M, (b) 0.05M (c) 0.075M, (d) 0.1M, (e) 0.15M, (f) 0.2M. Gas condition is air open. The bar indicate a 5nm scale. The magnifications were used to obtain the HRTEM images: X400000

5. Conclusion

A novel method for the preparation of Pt/C nano particles is reported. We have shown a controlled sized and homogenous distribution of the nano particles by this method. The RRDE and results showed a H_2O_2 formation rate is less than 3 % in the catalyst by this method and is very comparable to the commercial catalyst. It is required to increase the Pt loading in the optimized polyol process.

6. Reference

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