

Electrochemical Characterization of Metal Nanoparticles Electrodes as Fuel-cell Catalysts Prepared by using Various Solvents

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ABSTRACT: The crystalline sizes and loading efficiencies of metallic nanoparticles for fuel cell catalysts have been measured by changing solvent species. By changing solvent species containing carbon particles and metal salt precursors, the microstructure and the relating electrochemical property of catalysts could be controlled. Pt catalyst prepared by using EG solution showed the highest deposition efficiency, 85% and smallest crystalline size, 2.85 nm of catalysts, resulting a high activity. In the result, the electrochemical performance of catalysts was dependent on the crystalline size and deposition efficiency of catalysts with changing solvents.

Keywords: electrochemical properties, composite electrodes, preparation method, solvent systems, fuel cells

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) are attracting much more attention for their potential as clean and mobile power sources in the near future [1-5]. The use of methanol as a fuel has several advantages in comparison to hydrogen gas; it is a cheap liquid fuel, easily handled, transported, and stored, and with a high theoretical energy density. Another advantage of the DMFC is the fact that it does not require complex humidification and heat management modules as in the hydrogen fed proton exchange membrane fuel cell (PEMFC) system. The dilute methanol circulating the DMFC provides the necessary humidification and heat managements.

One of the major problems, which degrades the efficiency of conversion of the chemical energy of the methanol fuel to electrical energy in a DMFC, is the methanol crossover through the polymer electrolytes. The problem of methanol crossover in DMFCs could be studied by adopting new kinds of polymer electrolyte membrane and more stable catalysts. In other words, the problems could be solved either by using electrolyte membranes with lower methanol permeability or by developing new cathode electrocatalysts with both higher methanol tolerance and

higher activity for oxygen reduction reaction. [6-8]

On the other hand, it is reported that a particle size and a distribution of Pt-based catalysts are key factors that determine their electrochemical activity and cell performance for DMFCs [9-11]. However, the effects of the preparation method and the relationship between the structure and electrochemical performance of the prepared catalysts have not fully studied to our best knowledge.

Beside, a study is undertaken to explore the physicochemical effects of a variety type of carbon-supported metallic particles on the electrocatalytic oxidation of methanol when compared with a traditional supports medium, carbon blacks [12].

The objective of this study is to investigate the solvent effect of preparation method on the structure and loading efficiency of catalysts. Furthermore, structural effect of catalysts was studied on the electrochemical properties of the carbon-supported metallic nanoparticles. The crystalline sizes and loading efficiencies of metallic nanoparticles have been measured by changing solvent species. By changing solvent species containing carbon particles and metal salt precursors, the microstructure and the relating electrochemical property of catalysts could be controlled.

2. EXPERIMENTAL

2.1 Electrode preparation

Carbon-supported platinum catalysts were prepared by using a modified polyol synthesis method as reported before. 125 mg of carbon blacks was suspended in 25 ml of four kinds of solution and stirred with ultrasonic treatment for 20 min. The solution is water, tetrahydrofuran (THF), ethanol (EtOH), and ethylene glycol (EG).

4.0 ml of hexachloroplatinic acid ethylene glycol solution (58.3 mg H_2PtCl_6) was added dropwise to the solution under mechanically stirred conditions for 4 h.

NaOH was added to adjust the pH of the solution to about 13. Borohydride was added to the solution to reduce Pt at 120°C for 1.5 h, and a flow of argon was passed through the reaction system to isolate oxygen and to remove organic by products. The solid was filtered and washed with 2L of deionized water and then dried at 70°C for 8h. The final solid consisted of Pt deposited on the carbon blacks supports.

2.2 Characterization

All of the Pt-based carbon catalyst (Pt/C) samples were characterized by recording their X-ray diffraction (XRD) patterns on a Rigaku X-ray diffractometer (Model D/Max-III B) using Cu K α radiation with an Ni filter. Pt loading content was measured using Jobin-Yvon Ultima-C Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). The loading efficiency was obtained from the ratio of finally deposited Pt mass against the initially injected Pt mass.

To check an electrocatalytic activity of catalysts, linear sweep voltammetry method for a three-electrode cell system for obtaining current-voltage characteristic curves was performed. A working electrode was prepared by coating the catalyst powder mixed with Nafion® polymer onto a glassy carbon electrode. The carbon-supported metal catalyst particles were carefully introduced onto substrates.

One molar methanol in 0.5 M H_2SO_4 was used as an electrolyte solution. Cyclic voltammetry was studied by using a potentiostat/galvanostat of AUTOLAB/PGSTAT30 (Eco Chemie, Netherlands). A potential was changed linearly from 300 mV to 1100 mV vs. Ag/AgCl. The scan rate for sweeping potential was 20 mV/sec. Finally, the catalytic activity was obtained by calculating the current density at 1000 mV vs. Ag/AgCl by referencing the deposited Pt weight.

3. RESULTS AND DISCUSSION

3.1 Microstructure of catalysts

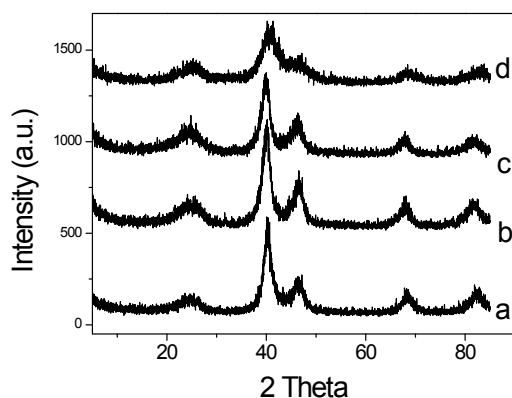


Figure 1: XRD patterns of Pt catalysts prepared using a organic solvent: (a) H₂O, (b) THF, (c) EtOH and (d) EG.

The powder XRD patterns for carbon blacks-supported Pt catalysts are shown in Figure 1. Figure 1 shows that Pt deposited on carbon supports forms a face centered cubic (fcc) structure and has four peaks such as peak (i) at $2\theta = 39.7^\circ$ (111), peak (ii) at 46.2° (200), peak (iii) at 67.4° (220) and peak (iv) at 81.2° (311). The broader diffraction peaks for the catalysts also lead to a smaller particle size that was calculated by the Scherrer equation [3,13]. The average crystalline size of Pt catalysts was estimated and presented in Table 1.

The sharpening of the XRD peaks indicates an increase of the average crystallite size with changing the solvent species. As a result, the catalyst using the water and THF shows a rather sharp crystalline peak, meaning that the prepared Pt particles have an larger average sizes.

In the case of using EG solvent, it was the condition for obtaining the small size of Pt nanoclusters of 2.85 nm. Pt using THF solvent shows the large size of Pt nanoclusters of 4.97 nm. Beside, the catalyst loading efficiencies were obtained independently by ICP-AES methods and

were shown in Table 1. Loading efficiency was obtained by the ratio of final Pt mass against the initially injected Pt mass. Pt using EG solvent shows the higher efficiency, 85%, whereas Pt using THF solvent the lowest efficiency, 56%. It indicates that the catalyst deposition was more favourable in the case of using EG solvent. This is probably related with that some parts of EG solvent species could function as a secondary reducing agent for Pt deposition. Of course, the primary reducing agent for Pt deposition is borohydride. For other samples, the solvent species could not afford any favourable function for Pt deposition. They could function as an only medium for dispersing the carbon particle and metal salt precursors. It is therefore concluded that the average sizes and loading efficiencies of Pt nanoclusters is strongly dependent on the reducing characteristics of solvent species.

Table 1: Crystalline sizes and loading efficiencies of Pt particle catalyst prepared by using a variety of solvents.

Solvent	Size (nm)	Loading eff. (%)
H ₂ O	4.12	69
THF	4.97	56
EtOH	3.36	78
EG	2.85	85

3.2 Electrochemical property of catalysts

Figure 2 shows current-voltage curves of Pt catalysts in 0.5 M H₂SO₄ containing 1.0 M CH₃OH. Pt prepared by using EG solvent showed the best electroactivity among the

samples due to its highest current density of anodic peak. This shows the Pt prepared by using EG solvent has a high activity towards methanol oxidation. Anodic peaks of methanol oxidation are observed at about 750 ~ 850 mV. The specific current density of anodic peak was greatly enhanced in this case, thus leading to higher electroactivity, when it was compared to other samples. However, in the case of using THF or EtOH, the catalysts show the rather small current density, resulting in poor electro-catalytic activity. This was related with the large particle size and ineffective deposition of catalysts. From this result, it was concluded that the high electro-catalytic activity was achieved when the catalyst was prepared by using EG solvent.

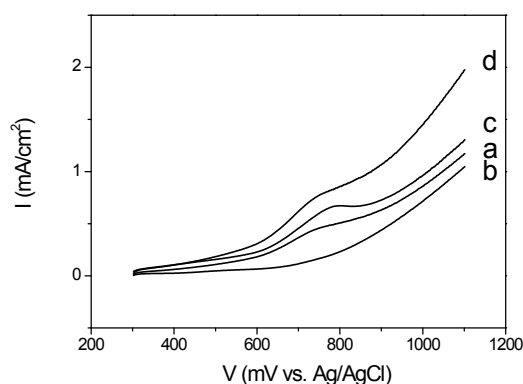


Figure 2: Current-voltage curves of Pt catalysts prepared using a organic solvent: (a) H₂O, (b) THF, (c) EtOH and (d) EG.

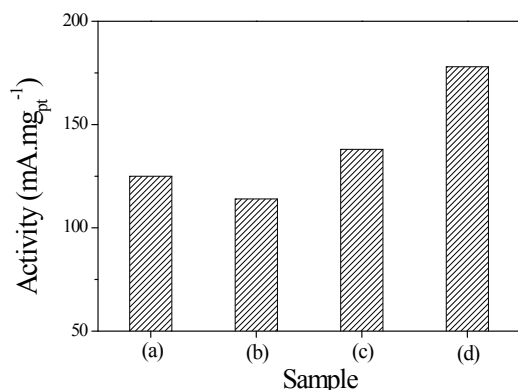


Figure 3: Electrochemical activities of Pt catalysts prepared using a organic solvent: (a) H₂O, (b) THF, (c) EtOH and (d) EG.

For analysing the catalyst activity more quantitatively, the activity was calculated on the basis of platinum weight. The activity was obtained from the current density at the same potential of 1000 mV for each sample. The activity was demonstrated in Figure 3. The catalyst activity was inversely proportional to the sizes of catalyst particles. It could be concluded that the electrochemical performance of catalysts was dependent on the crystalline size and deposition ability of catalysts. By controlling the nature of solvent species, the crystalline size and loading efficiencies could be changed.

4. CONCLUSION

The effect of solvent species containing carbon supports and metal precursor on the microstructure and electrochemical activity of Pt nanoclusters were investigated. Pt catalyst prepared by using EG solution showed the highest deposition efficiency, 85% and smallest crystalline size, 2.85 nm of catalysts. Pt by using THF solution showed the lower efficiency, 56% and larger size, 4.97nm.

Accordingly, Pt catalysts deposited on carbon blacks by using EG solution showed the highest current density for methanol oxidation. Finally, they showed the high catalytic activity, 178 mA/mg-Pt for methanol oxidation. This was primarily attributed to the rather small size and better deposition ability of particle catalysts, resulting an increased specific surface area for electrochemical reaction.

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