ELECTROCHEMICAL BEHAVIORS OF METAL NANOPARTICLES-ELECTRODES DEPOSITED ON CARBON COMPOSITES

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Introduction

Direct methanol fuel cells (DMFCs) are attracting much more attention for their potential as clean and mobile power sources in the near future. 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. However, the effects of the preparation method and the structure of various carbon materials have not fully studied to our best knowledge.

On the other hand, the unique properties of graphite nanofibers (GNFs) have generated an intense interest in an application of these new carbon materials toward a number of applications including energy storage, a polymer reinforcement, and catalyst supports. Recently, a study is undertaken to explore the physicochemical effects of GNFs-supported metallic particles on the electrocatalytic oxidation of methanol when compared with a traditional supports medium, carbon blacks. It is expected that the GNFs supported metallic particles have a high electrical conductivity and a good metal dispersion due to a highly ordered structure.

The objective of this study is to investigate the structural effect of binary carbon supports consisting of GNFs and CBs on the electrochemical properties of the carbon-supported metallic nanoparticles. The sizes and loading levels of metallic nanoparticles have been measured by changing the mixing ratio of two types of carbon materials. By changing the mixing ratio of GNFs/CBs, the specific surface area and the morphological structure of the mixed carbon materials are controlled.

Experimental

Carbon-supported platinum catalysts were prepared by using a modified polyol synthesis method as reported before. Graphite Nanofibers and carbon blacks with a changing mixing ratio were suspended and stirred with ultrasonic treatment for 20min in ethylene glycol (EG) solution and then a hexachloroplatinic acid (H_2PtCl_6)+ ruthenium chloride ($RuCl_3$)/EG solution was added dropwise slowly to the above solution and stirred mechanically for 4h. A 1.0M NaOH solution was added to adjust the pH of the solution to above 13, and then the solution was heated at 140°C for 3h for complete reduction of Pt. The whole preparation process was conducted under flowing Argon gas. The solid was filtered and washed with 2L of deionized water and then dried at 70°C for 8h.

By XRD experiments, we could obtain the average crystalline size of Pt nanoparticles by using Scherrer equation. Besides, Pt loading contents was measured by using EDS (Energy Dispersive X-ray Spectroscopy) methods.

To check the electrocatalytic activity, I-V characteristic curves were obtained by using cyclic voltammetry. We had prepared a working electrode by coating the catalyst powder mixed with Nafion polymer onto glassy carbon electrode.

Results and discussion

Fig.1 shows the SEM micrograph of graphite nanofibers (GNFs), which are used as a support for PtRu nanoclusters catalysts. The diameter of GNFs is in the range of 70 - 200 nm. These GNFs have a large aspect ratio of >3000 and a high electrical conductivity of $10^{-2} – 10^{-1}$ Ohm/cm due to the well-ordered graphitic structure. We have prepared the mixed carbon supports that consist of graphite nanofibers and carbon blacks. The samples were assigned as GNF0, GNF10, GNF30, GNF50, and GNF100 by changing the GNF weight ratio of 0, 10, 30, 50, and 100%.

After PtRu incorporation into carbon materials, the average crystalline sizes of nanoclusters were obtained by XRD measurements. The average size was increased from 3.58 nm to 6.41 nm gradually by changing the GNF content from 0% to 100%. The increase of Pt average size could be related to the decrease of specific surface area by increasing the portion of GNFs that have the smaller surface area rather than CBs.

Platinum content can be calculated by comparing the peak intensity of Pt against that of carbon from the EDS method. Pt loading content increased to 98% with the increase of GNF content upto 30%. However, further increase of GNF content has brought the decrease of Pt loading content. The electrochemical activity will be discussed in detail.

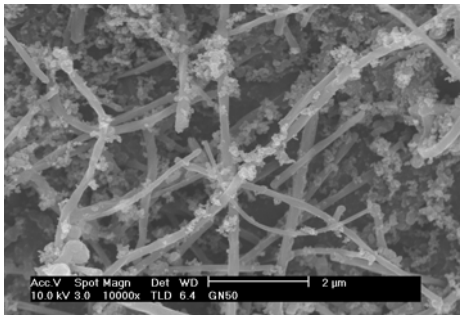

FIGURE 1: SEM micrograph of PtRu catalyst deposited on the binary carbon support of GNFs and CBs. (50:50 wt.ratio)

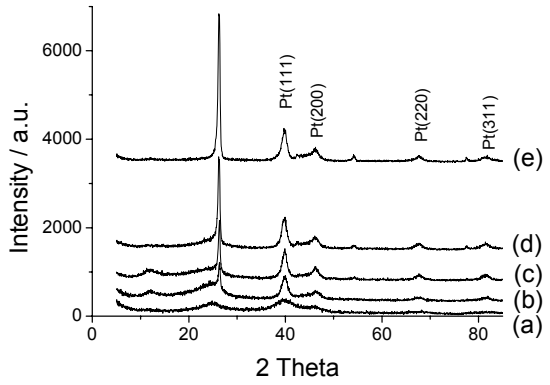

FIGURE 2: Powder X-ray diffraction patterns of PtRu catalysts deposited on (a) GNF0, (b) GNF10, (c) GNF30, (d) GNF50, and (e) GNF100

Conclusions

The metal catalysts were deposited on the mixed carbon support materials. By changing the ratio of GNFs and CBs, the particle size and deposition level were controlled. Electrochemical activities of metallic electrocatalyst deposited on the binary carbon supports with a changing ratio of GNFs and CBs had also been studied. The catalytic activity is probably related to the condition of carbon specific surface area and pore structure by controlling the mixing ratio.

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