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Investigation of electrocatalytic activity and stability of Pt@f-VC catalyst prepared by in-situ synthesis for Methanol electrooxidation

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ABSTRACT

The acidified, functionalized carbon black supported Pt nanocatalyst (Pt@f-VC) was prepared by the modified ethylene glycol reduction method. The functionalized carbon black serves as a stabilizer to prevent agglomeration of the platinum nanoparticles and ensures that Pt NPs have superficially greater dispersion. The prepared nanoparticles have been characterized by Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD), Raman Spectroscopy (RS) etc. XRD and TEM results showed that Pt NPs have uniform distribution on functionalized carbon support and the average particle sizes of Pt NPs were measured as 3.5 nm. Methanol electrooxidation reaction results showed that Pt@f-VC catalyst has higher catalytic activity and surface area than Pt@VC and commercial available Pt/C (Pt E-TEK).

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Introduction

Nanotechnology is providing fuel cell manufacturers with the technology needed to make fuel cells more durable and cost competitive with traditional power sources [1–3]. Today, although there are many alternative energy sources, direct alcohol fuel cells (DAFCs) are notable for variety of applications as significant electrochemical energy conversion systems. DAFCs are used as alternative energy sources because of their superior features such as low air pollution, applicability in room conditions and high energy conversion efficiency [1–6]. But one of the biggest challenges in the commercialization of DAFCs is its low anode performance, and scientists continue to develop various catalysts to come up with this

problem [7–10]. The other problem is that the activity of the catalyst depends on many factors such as particle size [11], particle morphology [12,13] and high metal catalyst concentration [14,15]. Generally Pt based nanoparticles (NPs) are preferred because of their small particle size, high dispersibility and easy connection to support materials [16–19]. In addition, Pt nanoparticles exhibit the highest electrocatalytic activity against methanol electrooxidation. However, there is a need for supporting materials to increase electrical conductivity and performance, lower the cost of the catalyst, and commercialize the catalyst. For this purpose, Vulcan carbon (XC-72), which has a high specific surface area, is an example of support materials frequently used in catalyst synthesis. Vulcan carbon selected as a support material for methanol electrooxidation has helped to uniformize the size

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of the Pt nanoparticles and help preserve the particle size. In addition, support materials are used due to the extraordinary mechanical properties such as thermal stability and good corrosion resistance since the life and performance of DMFCs are reduced due to corrosion of Pt NPs and poisoning due to organosulfur contaminants [20–24]. Although there are a number of studies of Pt-based catalysts on methanol oxidation with various carbon support materials, the studies comparing the performance of XC-72 as a supporting material are rare [25–33]. Besides, the functionalization of the carbon derivatives provides various possibilities to improve the usage of the carbon and to provide more chemical conversion to the carbon black. For this reason addressed herein, the functionalization of XC-72 was performed to increase the active surface, electrical conductivity, heterogeneous electron transfer rate of carbon black and homogeneous distribution of Pt-NPs on support was achieved. As a result of electrocatalytic investigations, it was observed that the electrooxidation of methanol of Pt@f-VC exhibited higher catalytic activity than Pt@VC and commercially available Pt-EOTEK. In this work, ethylene glycol (EG) -sodium borohydride (NaBH_4) reduction method was used to synthesize new Pt@f-VC catalysts and techniques such as TEM, XRD, XPS and Raman spectroscopy were used for the physical characterization of the synthesized catalyst. TEM, XPS, RS and XRD measurements have shown that the supportive carbon material significantly affects the morphology and electronic structure of Pt NPs. Furthermore, by the help of electrochemical measurements, it was also realized that the Pt@f-VC catalyst had higher electrocatalytic efficiency and stability for methanol electrooxidation compared to Pt@VC and commercially available Pt/C catalysts. These results show that the functionalized carbon supported Pt material has excellent activity as an anode catalyst.

Experimental

Acidic functionalization of Vulcan carbon

The synthesis of the Pt@f-VC nanocatalyst was carried out by the ethylene glycol- NaBH_4 reduction method and was named as “Pt@f-VC” after its synthesis. Prior to the synthesis step of the catalyst, the functionalization of the support material Vulcan carbon (VC) was carried out. To accomplish, 0.5 g of Vulcan carbon powder was put inside a 500 mL flask and slowly added 45 mL of 5% concentrated HNO_3 and 15 mL of concentrated H_2SO_4 . In the next step, Vulcan carbon was mixed with these two different concentrated acids at 90 °C for 24 h with the aid of a heating magnetic stirrer. After the oxidation was carried out, centrifugation was carried out at 6000 rpm for 30 min to remove excess acid. The finally obtained vulcan carbon was washed several times with ultra pure water and acetone mixture and dried in vacuum at 100 °C. Thus, the first step of functionalization of the support material of the nanocatalyst was carried out.

Synthesis of Pt@f-VC nanocatalysts

The ethylene glycol- NaBH_4 reduction method is used for the synthesis of the acid-functionalized vulcanized carbon

supported nanocatalyst in a single step. After completion of the Vulcan carbon functionalization, the resulting f-VC was mixed with the platinum salt (PtCl_4) in ethylene glycol for 1 h in the ultrasonic bath and then the pH of the mixture was adjusted to 8 using 1 M NaOH solution. Then the mixture was refluxed for 2 h at 120 °C and NaBH_4 was added slowly. The obtained Pt@f-VC catalyst was further refluxed at 120 °C for 1 h and the temperature of the mixture was cooled to room temperature. After that this catalyst solution was centrifuged and washed with ethanol several times. The washed catalyst was dried in vacuum and stocked for use in methanol oxidation.

Results and discussion

Physicochemical characterization

XRD (X-ray diffraction) method is used to determine the location of the Pt@f-VC nanoparticle in space (x, y, z) and to understand the crystal structure of the crystal. The XRD patterns of the functionalized vulcan carbon supported platinum nanoparticles are shown in Fig. 1(a). The peak around 24.8° corresponds to the (002) plane of Vulcan carbon. The diffraction peaks which are located at 2θ value of 39.8; 46.2; 67.1; and 81.3° were assigned to (111), (200), (220) and (311) planes, respectively, characteristic of face centered cubic (fcc) crystal structure of platinum.

The Scherrer equation was used to calculate the average particle size using the Pt (220) value found in XRD as shown below. By the help of the following formula, the crystal particle size of the Pt@f-VC nanoparticles was found to be 3.43 nm.

$$t = \frac{0.9\lambda}{\beta \cdot \cos(\theta)} \quad (1)$$

In the equation;

- t = crystal (or layer) size,
- λ = the wavelength of the X ray (1.54056 Å),
- β = the full width at half maximum intensity of the peak,
- θ = the angle of diffraction.

Raman spectroscopy of the obtained Pt@f-VC and Pt@VC nanocatalysts are shown in Fig. 1 (b). Raman spectroscopy is a widely used spectroscopic method for the characterization of carbon species, especially due to conjugate and double carbon-carbon bonds causing high Raman intensity. Here, several prominent Raman peaks typical of carbon are observed. The well-known peaks of carbon were observed for all treated and untreated materials at various density and width levels at 1350 cm^{-1} and 1581 cm^{-1} , respectively. For the treated and untreated Vulcan carbon supported Pt nanoparticles we determined a ratio I_D/I_G of 1.63 and 1.42, respectively. The high density of the D band relative to the G band indicates a large amount of defects on the surface of carbon nanoparticles. We used this technique to observe that the vulcan carbon really functions.

The TEM image of the Pt@f-VC nanocatalyst is shown in Fig. 2(a). In the TEM image, the distribution of Pt NPs clearly

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