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Protein-based carbon and platinum nanocomposites as electrocatalysts for methanol oxidation activity

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ABSTRACT

Owing to the characteristics of high energy density, low operating temperature, and environmentally-friendly features, direct methanol fuel cells (DMFCs) are a promising renewable energy source. However, the electrocatalysts of the anode are vulnerable in terms of their electrochemical performance, as they can be easily toxified by CO and other hydrocarbons, which might lead to a break-up of the methanol oxidation reaction (MOR). For further advances in the DMFC industry with improved electrochemical performance, this issue should be urgently resolved. Thus, this study proposes a novel approach to synthesize protein-based carbon as platinum electrocatalyst supports (PCPs) from tofu using a carbonization for the improved methanol oxidation activities. Among commercial Pt/C and other samples, the composite loaded 10 wt% Pt electrocatalyst showed the highest anodic current density of 510 mA mg$_{Pt}^{-1}$, the excellent electrocatalytic stability, and the highest retention of 86%. The improved electrochemical performances can be attributed to the good dispersion of Pt electrocatalysts and N-doping effect of protein-based carbon supports. These results suggest that PCPs derived from tofu will be one of promising candidates as platinum catalyst supports to improve methanol oxidation activities.

1. Introduction

In recent years, the development of renewable power resources has become a key issue on the way towards realizing the global object of reducing consumption of fossil fuels and moving to new clean energy technologies. Due to their low operating temperature, high energy conversion, high energy density, and low emission of pollutants, direct methanol fuel cells (DMFCs) are nowadays a promising renewable energy source for airport baggage trucks, smaller boats, and torches [1–5]. The four main components of DMFCs include the anode, cathode, membrane, and electrolyte. During the operation, methanol oxidation reaction (MOR, $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$) occurs on the electrocatalysts of the anode that define the electrochemical performance and cost-effectiveness of DMFCs [6–10]. However, a weak point of DMFCs is that they mainly employ Pt electrocatalysts, which might lead to several important disadvantages, such as the high cost of Pt, inclination to agglomerate of Pt, and poor CO tolerance arising due to the accumulation of surface-adsorbed intermediate species, such as CO, CHO, and COOH. Among them, the use of high-priced Pt is the most significant challenge that hinders the industrial use of DMFCs [11–15].

To solve these problems, previous studies have sought to find strategies to enhance the efficiency of Pt electrocatalysts, such as the controlling the morphology, the introduction of support materials, and alloying them with various metals [16–18]. The introduction of support materials, such as metal/metal oxide, carbide, and carbon, is among the most promising strategies to minimize the loading of Pt electrocatalysts and enhance their electrochemical performance in DMFCs. In general, the latest DMFCs technology uses various carbon-based supports, such as graphite, carbon nanotubes, and carbon nanofiber, characterized by high electrical conductivity, excellent electrocatalytic stability, and high surface area [19–22]. However, to expand the DMFC industry, it is necessary to provide a better performance than the existing carbon supports.

Therefore, in the present study, we used a new carbon with

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protein for Pt electrocatalyst supports. Overall, while several oil- and biomass-based carbons for Pt electrocatalyst supports have been investigated to date, no research has been conducted on protein-based carbons. Accordingly, in the present study, we focused on proteins from tofu for Pt electrocatalyst supports. Tofu is a traditional Asian food consisting of 80 wt% water and 20 wt% protein. High protein content and few impurities makes it suitable for the use as a precursor of carbon [23–25]. In addition, since the amino acid constituting the protein contains nitrogen, N-doped carbon can be produced simultaneously. Recently, several studies demonstrated that heteroatoms doped carbon supports, particularly nitrogen, can improve the physical and electrochemical properties. The affluent free π electrons, inert for chemical reactions, are available in the carbon, making it a potential electrocatalyst material. The carbon π electrons can be activated because it conjoins with long-pair electrons from nitrogen dopants. In addition, it was found that the existence of N-doping can also introduce a chemically active site on the carbon support that acts as an anchoring site for Pt nanoparticles deposited on its surface with the synergistic interaction of Pt electrocatalyst and carbon support [25,26]. Therefore, these advantages of N-doped carbon derived from tofu can provide improved electrocatalytic activity and stability.

In the present study, we successfully fabricated protein-based carbon as Pt electrocatalysts supports and controlled the amount of platinum loading for the optimal electrocatalysts for the methanol oxidation activities.

2. Experimental

2.1. Chemicals

The tofu was purchased from Pulmuone Co., Ltd. (Korea). The chloro-platinic acid hydrate ($H_2PtCl_6 \cdot xH_2O$, ≥99.9%), sodium boron-hydride ($NaBH_4$), 2-propanol, Nafion perfluorinated resin solution, methanol (anhydrous, 99.8%), hydrofluoric acid (HF, ACS reagent, 52%), nitric acid (HNO_3 ACS reagent 66%), and sulfuric acid (H_2SO_4, ACS reagent, 70%) were obtained from Sigma-Aldrich. All chemicals were used without further purification.

2.2. Synthesis of protein-based carbon as platinum electrocatalysts supports

The protein-based carbon as Pt electrocatalysts supports were prepared by the carbonization. Firstly, the tofu was dried in an oven at 80 °C to eliminate any moisture, then heated at 300 °C to remove impurities, and, finally, carbonized at 800 °C for 2 h under the nitrogen atmosphere. The carbonized sample was acid-treated using a mixture (1:1 (v/v)) of HF and HNO_3 to form the functional groups on the surface. Thereafter, the ball mill was employed to obtain the nano-sized support. To fabricate the Pt electrocatalysts on the supports, the reduction method was used. The N-doped carbon support was dispersed in 0.14 mM, 0.28 mM, and 0.56 mM $H_2PtCl_6 \cdot xH_2O$ (≥99.9%) solution in deionized (DI) water and reduced by $NaBH_4$ to load 5, 10, and 20 wt% Pt electrocatalyst on the support, respectively. The obtained samples were washed several times in DI water and then freeze-dried at −50 °C to get the metallic Pt phases. Therefore, we successfully obtained the protein-based carbon as 5, 10, and 20 wt% Pt electrocatalysts supports (herein referred to as PCP-5, PCP-10, and PCP-20). The conventional Pt/C (20 wt% Pt on Vulcan carbon, De Nora S.P.A.) was used for comparison.

2.3. Characterization

The morphologies and structures of the samples were examined using field emission–scanning electron microscopy (FE-SEM, Hitachi S–4800) and transmission electron microscopy (MULTI/TEM; Tecnai G^2, KBSI Gwangju Center). The crystal structures and chemical bonding states of the samples were characterized by X-ray diffractometry (XRD, Rigaku D/Max 2500 V) with the Cu K_α radiation in the range from 10° to 90° with the step size of 0.02° and X-ray photoelectron spectroscopy (XPS, ESCALAB 250) with an Al K_α X-ray source. The binding energies of the XPS spectra were standardized to the C 1s core level (284.5 eV).

2.4. Electrochemical characterization

Electrochemical performance measurements were performed using a potentiostat/galvanostat (Ecochemie Autolab PGST302 N, Netherlands) in a conventional three-electrode system consisting of a the working electrode (glassy carbon electrode, area = 0.0706 cm^2), the counter electrode (Pt gauze), and the reference electrode (Ag/AgCl, sat. KCl). To investigate the methanol oxidation activities, all samples were mixed to inks of 80 wt% electrocatalysts and 20 wt% Nafion in 2-propanol. All inks were then carefully dropped on the glassy carbon electrode and dried at 60 °C. In the next step, the methanol oxidation activity tests were run using cyclic voltammograms (CV) in a 2 M CH_3OH and 0.5 M H_2SO_4 electrolyte between −0.2 and 1.0 V (vs. Ag/AgCl) at the scan rate of 50 mV s^{-1}. To examine the electrocatalytic stability and retention, chrono-amperometry (CA) was performed in a 2 M CH_3OH and 0.5 M H_2SO_4 electrolyte at the constant potential of 0.5 V for 2000s and 0.45 V for 7200s, respectively. For comparison, electrochemical performance measurements of commercial Pt/C were also performed under the same conditions.

3. Results and discussion

Fig. 1 illustrates the synthetic process for fabricating PCP-10. The tofu (see Fig. 1a) consisting of protein and water was dried to eliminate moisture and then heated at 300 °C to make calcined tofu (see Fig. 1b); therefore, tofu-based carbon supports were formed using ball mill and carbonization (see Fig. 1c). In addition, to form the functional group on the surface, we used acid treatment. Finally, PCP-10 (see Fig. 1d) was synthesized using the reduction method, implying that well-dispersed Pt electrocatalysts on the protein-based carbon were formed.

Fig. 2 shows the SEM images obtained from PCP-5, PCP-10, and PCP-20. The diameters of the samples amounted to ca. 254–311 nm for PCP-5, 221–315 nm for PCP-10, and 230–319 nm for PCP-20. All samples showed the semi-block morphology. To further examine the structural properties and morphological of the samples, TEM measurements were performed.

Fig. 3 shows low-resolution (Fig. 3a–c) and high-resolution (Fig. 3d–f) TEM images of PCP-5, PCP-10, and PCP-20. PCP-5 (see Fig. 3a and d) showed that Pt electrocatalysts were sparsely distributed on the protein-based carbon due to a small amount of Pt precursor when the reduction method was used. Among the samples, PCP-10 (Fig. 3b and e) exhibited an excellent dispersion of Pt electrocatalyst on the protein-based carbon and a relatively small amount of Pt agglomeration. In addition, PCP-10 indicated the nanosized Pt electrocatalyst particles (3–4 nm) and definite lattice fringes with the spacing of 0.22 nm, which were attributed to the (111) planes of Pt [3,22]. The excellent dispersion of nanosized Pt can provide the large electrochemical active sites, resulting in excellent electrocatalytic activity during the methanol oxidation. However, PCP-20 (see Fig. 3c and f) showed the agglomerated Pt