Platinum catalysts on KOH-treated multi-walled carbon nanotubes for PEM fuel cell nano sized dense structured electrodes

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In this study multi-walled carbon nanotubes (MWCNTs) were thermally treated in the presence of potassium hydroxide (KOH) at various temperatures and times and then applied as platinum (Pt) supporting materials for electrocatalysts. Pt was deposited on the MWCNTs using a colloidal method under microwave irradiation. The morphological properties of the Pt-MWCNTs were determined by transmission electron microscopy (TEM), and their electrochemical performance was evaluated using cyclic voltammetry (CV). The KOH-treated MWCNTs favored the dispersion of Pt nanoparticles with a narrow size distribution, and the Pt-MWCNT catalysts displayed excellent electrochemical performance. Notably, the electrochemical surface areas (ECSA) of the Pt-MWCNTs were higher than those of acid-treated Pt-MWCNTs. Moreover, the KOH-treated Pt-MWCNTs were more durable (measured in terms of CV performance) than the acid-treated Pt-MWCNTs. Thus, heat activation with KOH is an effective means of modifying MWCNT surfaces for use as Pt supporting materials with higher ECSA, making them suitable for use as electrocatalytic materials in proton exchange membrane fuel cells.

Key words: Carbon nanotubes, Electrocatalyst, microwave, Potassium hydroxide, Proton exchange membrane fuel cell.

Introduction

Carbon materials, including amorphous carbon, carbon nanotubes (CNTs), graphite, graphene, and fullerenes, have many applications in modern science [1]. CNTs, consisting of rolled up graphene-like sheets, have attracted particular attention for their use in chemical sensors, display materials, and catalysts of chemical reactions [2, 3]. They have several remarkable properties, including high tensile strength [4], high electrical conductivity [5], and chemical stability [6]. Among their many uses, CNTs can be applied as active electrocatalysts with platinum (Pt)-deposited structures in proton exchange membrane fuel cells (PEMFCs) [7, 8].

PEMFCs have potential for use in our future energy needs; they can be operated at low temperature in an environmentally friendly manner. In PEMFC systems, Pt-carbon structures act as an electrocatalytic layer for the redox reaction. Unfortunately, Pt is expensive and, during operation of a PEMFC, accelerated corrosion of the carbon support can lead to aggregation of Pt nanoparticles and subsequent loss of activity. For these reasons, many approaches have been tested with the goal of commercializing PEMFCs, including improving the durability of the devices [9-11]; replacing the Pt metal with other metal particles [12, 13]; using Pt-alloy structures [14]; controlling the shape and size of the metal particles [15-19]; and using metal-free catalyst structures [20].

When preparing Pt-CNT composite structures, pristine CNTs are often first treated through acid oxidation (e.g., sonication or refluxing in a mixture of HNO_3 and H_2SO_4) to form active sites on their surfaces [21]. These active sites behave as binding sites for immobilization of metal particles with improved particle dispersion. Surface treatment is also possible through heat treatment in the presence of potassium hydroxide (KOH) under an inert atmosphere. This approach can functionalize a carbon surface with oxygen-containing groups to improve the chemical surface area [22], thereby facilitating the access of the active phase during catalyst preparation, as well as enabling high catalyst dispersion. Nevertheless, KOH-activated CNT structures have not received much attention for application in fuel cell catalysts.

The aim of this study is to investigate the KOH activating effect of MWCNTs through the durability test of Pt-MWCNTs. MWCNTs were thermally treated with KOH at various temperatures and times and then adopted as Pt supporting materials for application as electrocatalysts. Subsequently, Pt deposition was performed using a colloidal method under microwave irradiation [23]. The morphological properties of the Pt-MWCNTs were determined by transmission electron microscopy (TEM); their electrochemical performance was evaluated through cyclic voltammetry (CV) and compared with those of acid-treated Pt-MWCNTs.

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Experimental Section

Materials

The MWCNTs had diameters of 7-12 nm and purity of greater than 99% (Sigma-Aldrich). KOH (95.0%, Samchun Chemicals) was used as the surface modification precursor. Etylene glycol (EG, 99.0%) and isopropyl alcohol (IPA, 99.5%) were purchased from Daejung. Hexachloroplatinate (IV) hydrate ($H_2PtCl_6 \cdot H_2O$) was obtained from Kojima Chemicals. All aqueous solutions were prepared using distilled water purified through an Eco-PO&UP system (Mirae Scientific Technology). H_2SO_4 (97%), HNO_3 (60%), and HCl (35-37%) were purchased from Samchun Chemicals. Nafion solution (5% in water/alcohol mixture) was obtained from DuPont.

KOH/Heat treatment of MWCNTs

Raw MWCNTs were physically mixed with KOH powder at a KOH-MWCNTs mass ratio of 4 : 1. After drying at 110 °C overnight in a high-temperature oven, the heat treatment process was performed in a furnace at either 800 or 900 °C for either 1 or 2 h under a N_2 flow (500 mL min^{-1}). The powder was cooled to room temperature and washed with HCl (5.0 M) for 30 min. The HCl solution was removed through centrifugation. The mixture was washed several times with DI water until its pH became neutral. Finally, the heat-treated MWCNTs were obtained after drying overnight at 40 °C in a vacuum oven.

Acid treatment of MWCNTs

Raw MWCNTs were treated with an acid solution [H_2SO_4/HNO_3, 3 : 1 (v/v)] with stirring for 5 min and sonicating for 2 h. The mixture was then heated under reflux at 90 °C for 2 h to remove any impurities and generate surface functional groups, following previously reported procedures [24]. The solution was isolated from the acid solution and then centrifuged (4000 rpm, 10 min) and washed three times with DI water.

Synthesis of Pt-MWCNTs

Pt-MWCNTs were prepared using a microwave-assisted colloidal method. A suspension of the treated MWCNTs (0.0325 g) in H_2O and IPA (9 : 1, v/v; 50 mL) was sonicated for 30 min. Pt precursor solution [hexachloroplatinate (IV) hydrate mixed with EG; 19 : 1, v/v; 0.858 g] was added to the suspension, followed by EG (150 mL). The pH of the system was adjusted to 8 through a dropwise addition of 0.5 M KOH solution; a well-dispersed slurry was obtained after stirring for 1 h. The slurry was heated in a microwave oven for 5 min and then the mixture was cooled to room temperature with stirring. After washing several times with EtOH and centrifuging, then vacuum drying, a black solid sample was obtained.

Coating electrodes with the catalyst

A Pt-MWCNT catalyst (0.005 g), Nafion solution (5% in EtOH; 0.06 mL), and IPA (0.5 mL) were mixed and sonicated for 10 min. A drop (30 μL) of the solution was placed on a Pt electrode and dried at room temperature for 15 min to fix the catalyst to the working electrode surface.

Characterization

Heat treatment was performed in a tube furnace (DTF-50300SH). The Pt weight percent was determined through thermogravimetric analysis (TGA, SDTQ600) while increasing the temperature at a rate of 10 °C min^{-1} from 30 to 900 °C under a continuous flow of air. Images of the Pt particles on the modified MWCNTs were recorded using TEM (JEM-2000EXII) under an accelerating voltage of 200 kV.

Electrochemical characterization was performed at room temperature through CV (GAMRY instruments Model Reference 3000) using a three-electrode system: a Pt electrode (diameter: 1 nm) as the working electrode, an Ag/AgCl electrode as the reference electrode, and Pt foil as the counter electrode. The cyclic potential was swept between -0.2 and + 1.2 V at a rate of 10 mV s^{-1}. Prior to measurement, the electrolyte (0.5 M H_2SO_4) was saturated with N_2 by bubbling with the gas for 30 min. Stable voltammogram curves were recorded after five cycles of scanning; potentials are provided versus a Ag/AgCl electrode.
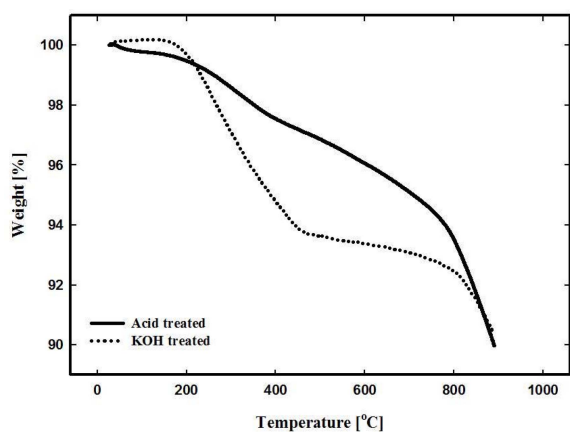
Results and Discussion

CNTs are widely recognized for catalyst supporting materials because of their high mechanical strength and conductivity. Their nanostructures and broad surface areas facilitate the decoration of metal particles on their side walls. Although metal-CNT structures have good activity and selectivity in oxygen reduction reactions (ORRs) it can be difficult to attach metal particles onto CNTs without surface modification. Another important issue is the dispersion of the CNTs. Without surface modification, CNT bundles aggregate as a result of mutually attractive surface interactions. Accordingly, it is necessary to functionalize CNT surfaces through acid or KOH treatment to develop oxygen functional groups that facilitate chemical interactions between the anchoring catalyst metal ions and the modified CNT surfaces as well as increase the dispersibility. In this study, we treated MWCNTs at 800 and 900 °C for 1 and 2 h in the presence of KOH to effect surface modification.

Fig. 1 is an illustration that shows the difference of the formed functional groups of acid-treated MWCNTs and KOH-treated MWCNTs as reported in the work of Chaoxing et al. [25]. More functional groups on surfaces of KOH-treated MWCNTs benefit from stabilizing metal nanoparticles by a strong attractive interaction between
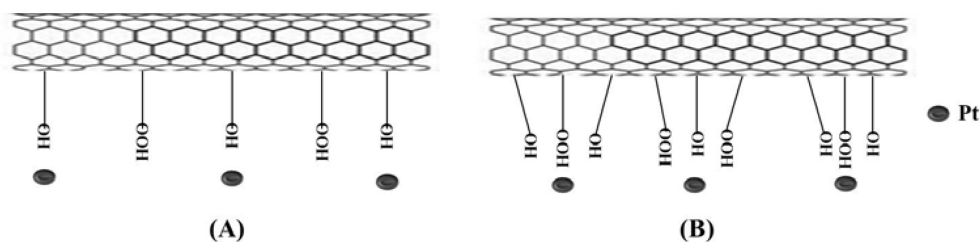
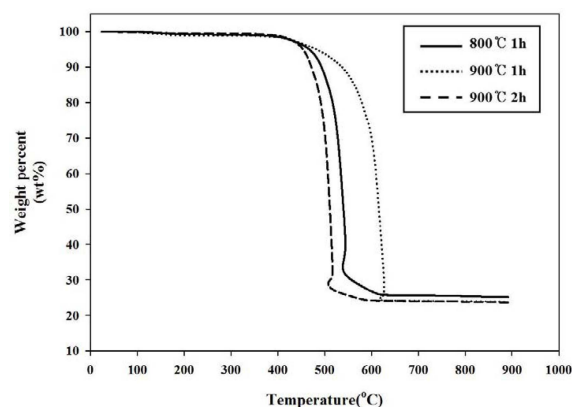**Fig. 1.** Illustration of Acid treated MWCNT(A) and KOH treated MWCNT (B).

Fig. 2. TGA results for Acid treated and KOH treated MWCNTs.

Fig. 4. TGA data of KOH-treated Pt-MWCNTs (800 $^{\circ}$C 1 h, 900 $^{\circ}$C 1 h and 900 $^{\circ}$C 2 h).

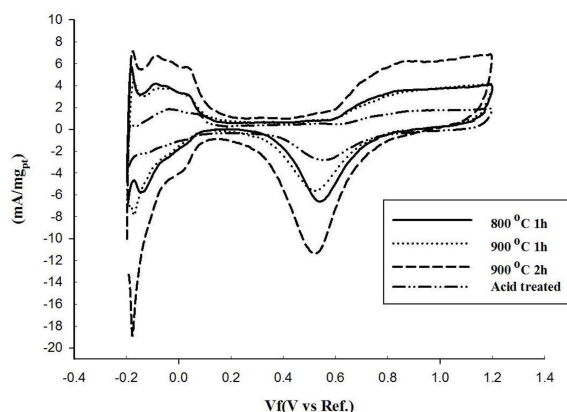**Fig. 5.** CV performance of KOH- and acid-treated Pt-MWCNTs.

the surrounding oxygen atoms.

In order to investigate the difference of carbon defect sites between acid-treatment and KOH-treatment, TGA was carried out under N_2 atmosphere. Because the carbon defect sites degrade at 200 to 400 $^{\circ}$C, the weight loss of the modified MWCNTs could be attributed to the amount of functional group formed on the MWCNTS. In the case of the acid treated MWCNTs, there is an approximately 2wt% of weight loss in 200-400 $^{\circ}$C, while KOH treated MWCNTs, 5 wt% of weight loss is observed in same temperature range. From TGA results it can be deduced that KOH-treatment method forms more functional groups on MWCNTs than acid-treatment.

EG is used in the Pt deposition process as a reducing agent because it has a high dielectric constant and a high reducing power [26]. At elevated temperatures, EG decomposes homogeneously and behaves as an agent for metal ion reduction [27]. To deposit Pt particles on CNT
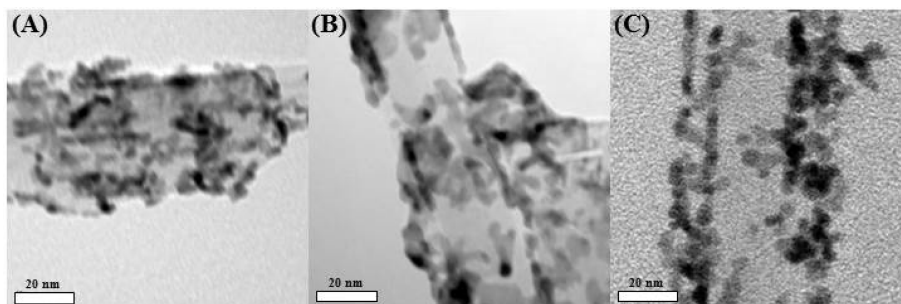
walls, it is essential to give the solution some energy (e.g., through heating). For this study we used microwave irradiation as a heating source. CNT bundles, especially their π-conjugated sectors, are good microwave absorbents

Fig. 3. TEM image of KOH- treated Pt-MWCNTs: (A) 800 $^{\circ}$C 1 h, (B) 900 $^{\circ}$C 1 h, (C) 900 $^{\circ}$C 2 h.

for use in the Pt deposition process. The mechanism for the immobilization of Pt nanoparticles in an aqueous EG solution is described by the following equations:

$$2CH_2OHCH_2OH \longrightarrow 2CH_3CHO + 2H_2O$$
$$2CH_3CHO + (PtCl_6)^{-2} + 6OH^- \longrightarrow 2CH_3COO^-$$
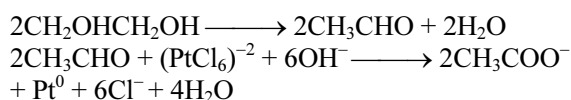$$+ Pt^0 + 6Cl^- + 4H_2O$$

Fig. 3 presents the TEM data of KOH-treated products. It reveals that the Pt particles were deposited uniformly on the CNT surfaces with narrow size distributions. TGA was used to measure the Pt weight percentages (wt%) in our samples. As shown in Fig. 4, all of our samples (800 ºC 1 h, 900 ºC 1h and 900 ºC 2 h) had Pt loadings of approximately 20 wt%. To study the electrochemical properties of KOH_treated Pt-MWCNTs (800 ºC 1h, 900 ºC 1 h and 900 ºC 2 h) electrocatalysts, we performed electrochemical measurements using a three-electrode cell.

Fig. 5 displays the CV performance, from -0.2 to + 1.2 V, of KOH-treated Pt-MWCNTs (800 ºC 1 h, 900 ºC 1 h and 900 ºC 2 h) and acid-treated Pt-MWCNTs in 0.5 M H_2SO_4 saturated with N_2 gas. To measure their electrochemical surface area (ECSA) we used the hydrogen adsorption peak and the following equation [28]:

$$ECSA = \frac{Q_H}{m \times q_H}$$

Where Q_H is the charge for hydrogen desorption, m is the Pt metal loading, and q_H is the charge required for desorption a monolayer of hydrogen from the Pt surface. Table 1 summarizes the ECSAs of the KOH- and acid-treated Pt-MWCNTs. Increasing the temperature and time improved the electrochemical performance of the Pt-MWCNT catalysts, with the 900 ºC 2 h KOH-treated products being more active than the acid-treated Pt-MWCNTs.

To determine the durability of KOH-treated Pt-MWCNTs, 200 cycles of CV at a scan rate of 50 mV s^{-1}

**Table 1.** ECSAs of Pt-MWCNTs at various KOH treatment conditions.

	Pt-MWCNT (800 ºC 1 h)	Pt-MWCNT (900 ºC 1 h)	Pt-MWCNT (900 ºC 2 h)	Pt-MWCNT (acid treated)
ECSA	36.24 m^2/g	37.8 m^2/g	71.9 m^2/g	48.13 m^2/g
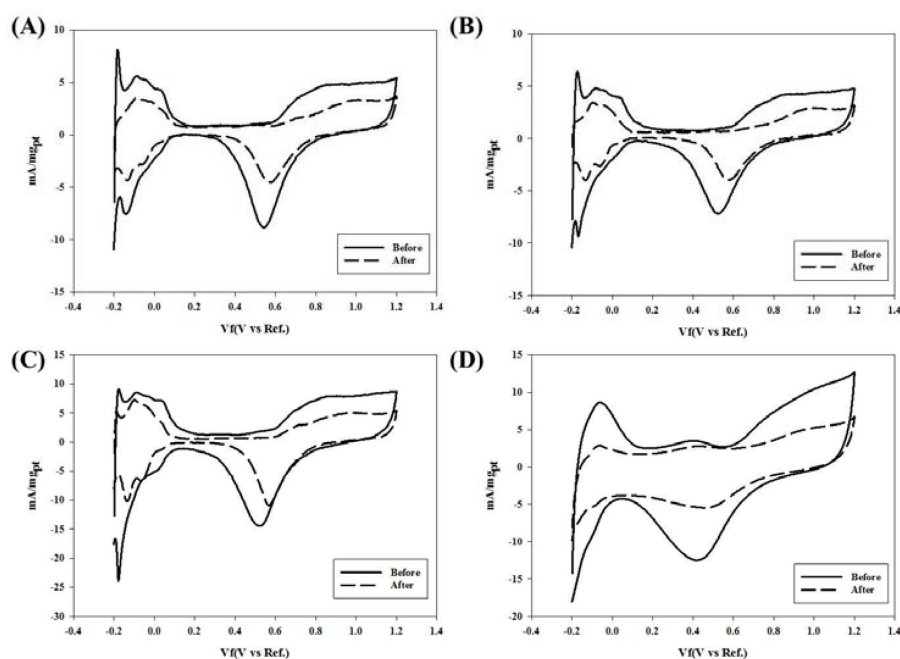
Fig. 6. Durability tests (CV, 200 cycles) of KOH-treated Pt-MWCNTs: (A) 800 ºC 1h, (B) 900 ºC 1h, (C) 900 ºC 2 h, and (D) Acid-treated Pt-MWCNTs.

Table 2. The ECSA values of durability test(before and after).

	Pt-MWCNT (800 ºC 1 h)	Pt-MWCNT (900 ºC 1 h)	Pt-MWCNT (900 ºC 2 h)	Pt-MWCNT (acid treated)
ECSA (before)	36.24 m^2/g	37.8 m^2/g	71.9 m^2/g	48.13 m^2/g
ECSA (After)	21.3 m^2/g	20.3 m^2/g	51.4 m^2/g	25.19 m^2/g
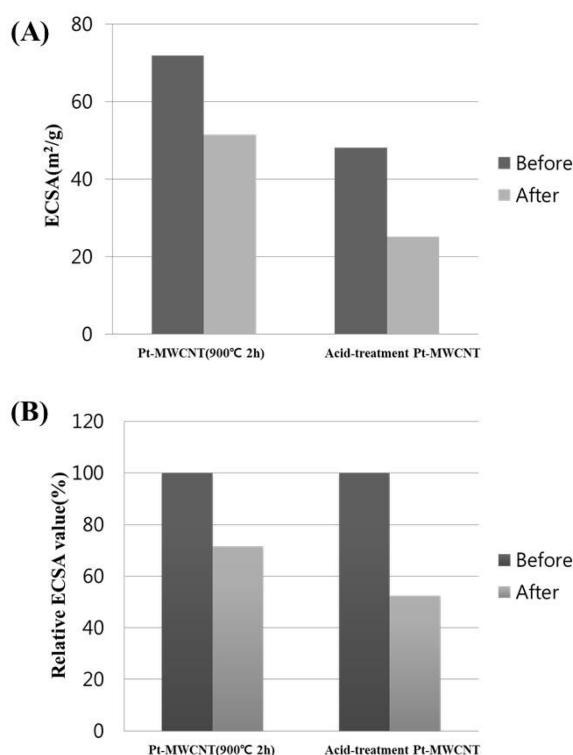
Fig. 7. Plots of (A) ECSAs and (B) relative ECSAs of KOH-treated Pt-MWCNT (900 °C 2 h) and an Acid-treated Pt-MWCNT.

were performed and compared the results with those of an acid-treated Pt-MWCNTs (Fig. 6); Table 2 summarizes the ECSAs of before and after 200 cycles of CV test. In these analyses, all the samples exhibited loss of activity as a result of agglomeration of the Pt particles. Among KOH-treated Pt-MWCNTs, the activity of the sample treated at 900°C for 2 h was greater than that of the acid-treated Pt-MWCNT; its ECSA decreased from 71.9 to 51.4 m^2 g^{-1} during the durability test. Fig. 7 reveals that the heat treatment process had a positive influence on the activity and durability of KOH-treated Pt-MWCNT (900 °C 2 h) relative to those of the acid-treated Pt-MWCNT.

Conclusions

In this study, MWCNTs were treated with KOH at various temperatures and times (800 °C for 1 h, 900 °C for 1 h, 900 °C for 2 h). TG data revealed that KOH-treatment method made more functional groups than acid-treatment method. For use as fuel cell catalysts, Pt nanoparticles were deposited, through a colloidal process, onto the surfaces of KOH-treated MWCNTs. TEM analysis showed that the Pt nanoparticles had been deposited with narrow size distributions on the modified MWCNTs. In measurements of the electrochemical performance of the electrodes, CV tests unveiled (from ECSAs) that KOH-treated Pt-MWCNTs were more active than acid-treated Pt-MWCNTs. Durability tests, performed

through 200 cycles of CV, revealed that, among KOH-treated Pt-MWCNT products, the sample treated at 900 °C for 2 h had greater initial and terminal ECSAs than an acid-treated Pt-MWCNT. Thus, heat activation in the presence of KOH appears to be an effective method for modifying MWCNT surfaces for use as Pt support materials with high ECSAs, making them more suitable for PEM fuel cell applications as electrocatalytic materials.

Acknowledgments

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