



Synthesis of highly dispersed platinum/carbon catalyst using cetyltrimethyl ammonium bromide as a dispersant for proton exchange membrane fuel cells

Rong-Hsin Huang^a, Wen-Kai Chao^a, Ruei-Sung Yu^b, Kan-Lin Hsueh^{c,*}, Fuh-Sheng Shieu^{a,*}

^a Department of Materials Science and Engineering, National Chung Hsing University, Taichung 40227, Taiwan

^b Department of Photonics and Communication Engineering, Asia University, Taichung 41354, Taiwan

^c Department of Energy Engineering, National United University, Miaoli 36003, Taiwan

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ABSTRACT

The highly dispersed platinum/carbon (Pt/C) catalysts with excellent activity were synthesized using an impregnation method with cetyltrimethyl ammonium bromide (CTAB) as a dispersant. The catalysts were then calcined at 300 °C under high vacuum to remove CTAB. The calcination temperature used was lower than the high temperatures (≥ 500 °C) typically used for removing surfactants in nitrogen or argon. The high vacuum pressure prevents the aggregation and oxidation of Pt nanoparticles. Transmission electron microscopy results showed that the Pt nanoparticles, which had average sizes of 2.0, 2.3, and 2.7 nm at CTAB concentrations of 1.37×10^{-2} , 2.75×10^{-2} , and 4.12×10^{-2} M, respectively, were well dispersed on carbon black. Thermogravimetric analyses indicated that the Pt/C catalysts content increased with increasing CTAB concentration. Cyclic voltammetry analyses confirmed that the electrochemically active surface area and long-term stability of the Pt/C catalysts were better than those of commercial 20 wt.% Pt/C catalyst. The Pt/C-4.12 catalyst performed exceptionally well; the power density of a single cell was 40.9% and 45.4% higher than that of a commercial one at operating cell temperatures of 25 and 75 °C, respectively. The results show that Pt/C catalysts synthesized from this method have promising applications in proton exchange membrane fuel cells.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs), which use hydrogen and oxygen as fuels, have been recognized to be the most promising candidates for a wide range of applications in transportation and home and portable devices [1,2]. PEMFCs have near-zero pollutant emissions, high power density, high energy conversion efficiency, and simplicity of operation that far exceed those of conventional internal combustion systems that use fossil fuels [3–5]. Considerable efforts have been made to commercialize PEMFCs. However, a number of key challenges have yet to be overcome. The Pt utility efficiency of platinum/carbon (Pt/C) catalysts has a direct influence on the performance of PEMFCs [6–9]. A Pt/C catalyst with a high utility efficiency aims to optimize the performance and durability of PEMFCs. Researchers have concentrated on improving the dispersal of Pt nanoparticles on carbon black (CB) to increase the Pt utility efficiency of Pt/C catalysts. An effective dispersion method would not only yield a Pt/C catalyst with a high utility efficiency but also reduce the quantity of Pt used,

and thereby reduce the overall cost of producing such catalysts. Various dispersion techniques, such as hydrothermal techniques [10], impregnation [6], sol-gel techniques [11], and the grafting of organics [9,12,13], each of which has been used extensively in the synthesis of nanoparticles, have been proposed. Furthermore, surfactants, such as tetraoctylammonium bromide (TOAB) [14], cetyltrimethyl ammonium bromide (CTAB) [15,16], and 3-(*N,N*-dimethyldodecylammonio) propanesulfonate (SB12) [7], which are used to form micelles and prevent the aggregation of nanoparticles, are key components in these dispersion methods. The adsorption of surfactants to the surface of a Pt/C catalyst would greatly reduce its activity. Thus, surfactants must be completely removed to maximize the effectiveness of the Pt/C catalyst, and calcination of the as-synthesized Pt/C catalyst at high temperatures (≥ 500 °C) [7,14,15] is the conventional approach with which to achieve this. Pt nanoparticles oxidize and aggregate easily at high temperatures with the potential to greatly reduce the utility efficiency of the Pt/C catalyst. In the literature, few studies have focused on the addition of CTAB for the dispersion of Pt nanoparticles on CB (XC-72) to improve the activity of the resulting catalysts. Song et al. prepared Pt/carbon hollow nanospheres catalysts using CTAB as a dispersant [16] that required calcination at 600 °C to remove the surfactant. Zhou et al. reported that CTAB could improve the wettability of mesoporous carbon and the dispersion of Pt nanoparticles [15].

* Corresponding authors. Tel.: +886 4 2285 4563; fax: +886 4 2285 7017.

E-mail addresses: kanlinhsueh@hotmail.com (K.-L. Hsueh), fsshieu@dragon.nchu.edu.tw, D9666210@mail.nchu.edu.tw (F.-S. Shieu).

In the current study, a commercially and readily available cationic surfactant CTAB was used as a dispersant to enable the excellent dispersal of the Pt/C catalyst. CTAB includes lipophilic alkyl and hydrophilic amine groups that are capable of suspending nanoparticles to form micelles or serve as linkers between the carrier and the metal ion via electrostatic interactions in aqueous solution. A significant attempt was made to reduce the surfactant removal temperature to 300 °C by exploiting the process of vacuum thermal-treatment to enhance the activity of the synthesized Pt/C catalysts. The crystal structure and composition of the as-received Pt/C catalysts were characterized using X-ray diffraction (XRD) and energy dispersive X-ray spectrometry (EDS). The influence of CTAB concentration on both the Pt nanoparticle size and the Pt loading of the Pt/C catalysts was analyzed using transmission electron microscopy (TEM) and thermo-gravimetric analysis (TGA). The formation of well-dispersed Pt nanoparticles and the Pt particle morphology of the Pt/C catalysts were analyzed using TEM and scanning electron microscopy (SEM). The activity and stability of the Pt/C catalysts were demonstrated using cyclic voltammetry (CV). A polarization test was used to investigate the performance of the Pt/C catalysts in the fuel cells. Single cells based on the Pt/C catalysts perform favorably compared with those produced using commercial catalysts (Johnson Matthey, JM-20 wt.-%-Pt/C) at operating temperatures of 25 and 75 °C.

2. Experimental

2.1. Preparation of the Pt/C catalyst

The 20 wt.-% Pt/C catalysts were synthesized by the impregnation method [6,17]. The method consists of following steps. First, 30 mL of cetyltrimethyl ammonium bromide (C₁₉H₄₂BrN, CTAB, Sigma, 99.9%) aqueous solution was prepared in the various concentrations of 4.12×10^{-2} , 2.75×10^{-2} , and 1.37×10^{-2} M. Second, each solution of different concentration was ultrasonically mixed with 1.0 g CB (Vulcan[®] XC-72, Cabot) for 30 min to obtain finely dispersed CB particles. Third, 0.663 g H₂PtCl₆·6H₂O (Alfa Aesar, 99.95%), 10 mL of 1 M NaOH, and 10 mL of methanol (EM-1001, 99.8%, ECHO, Chemical Co., Ltd.) were added to each aforementioned mixture to prepare the good dispersion of Pt/C catalysts using an impregnation method at 80 °C for 4 h. Fourth, the as-made Pt/C catalysts were filtered, washed with 50 mL of alcohol and 200 mL of deionized water, and then dried in a vacuum oven at a pressure of 101.32 Pa under 80 °C for 6 h. Finally, the as-made Pt/C catalysts were calcined in a vacuum oven at a pressure of 1.20 Pa from room temperature to 300 °C. The ripe deliberation of calcination temperature selected was based on the report of Wu et al. [18], who presented the oxidation temperatures of CTAB between 220 °C and 350 °C. Table 1 gives the quantity of CTAB used during the preparation of the Pt/C catalysts.

2.2. Physicochemical characterization of the Pt/C catalyst

The crystal structure of the Pt nanoparticles was analyzed using a MAC MXP III X-ray diffractometer with Cu K α radiation ($\lambda = 0.154$ nm, sweeping angle of $2\theta = 10$ – 90° , sweeping rate of 2° min^{-1}), and the diffraction peaks were compared with those in the JCPDS data file. The morphology and distribution of Pt

nanoparticles were examined using a field emission scanning electron microscope (FE-SEM, JEOL 6700, Japan) coupled with an X-ray energy dispersive spectrometer (EDS) operating at 15 kV, and a high-resolution transmission electron microscope (HR-TEM, JEOL 2100F, Japan) operating at 200 kV. The weight percentages of the Pt nanoparticles in the Pt/C catalysts were measured using a thermogravimetric analyzer (Perkin Elmer TG/DTA 6300, USA) at temperatures ranging from 25 °C to 800 °C with a $5^\circ \text{ C min}^{-1}$ ramp rate in air. Cyclic voltammetry (CV), which was used to analyze the electrochemically active surface area (S_{ESA}) of the Pt/C catalysts, was performed under ambient conditions with a scanning rate of 10 mV s^{-1} from -0.3 V to 1.2 V in $1.0 \text{ M H}_2\text{SO}_4$ solution, and the long-term stability of the Pt/C catalysts was operated at 0.6 V in $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{OH}$ solution using a CHI-614B (CH Instrument, USA) electrochemical analyzer and a standard three-electrode electrochemical cell. Ag/AgCl and a platinum wire were used as the reference electrode and counter electrode, respectively. The working electrode was prepared by coating the surface of a disk-type carbon electrode with Pt/C ink (Zensor R&D Co., Ltd.).

The electrode ink was prepared using 5 mg of Pt/C catalyst ultrasonically suspended with 50 μL of 0.5 wt.-% Nafion solution for 1 h. Approximately 10 μL of Pt/C electrode ink was spread onto the surface of a clean standard carbon electrode using a micropipette, and the electrode dried at 80 °C for 1 h in a vacuum oven at a pressure of $1.013 \times 10^3 \text{ Pa}$. The drying process assisted in fixing the Pt/C ink on the carbon electrode, resulting in a thin active layer with a Pt/C loading of $0.51 \mu\text{g cm}^{-2}$. The working electrodes were entirely activated to a steady state by 10 cycles in a $0.5 \text{ M H}_2\text{SO}_4$ solution at 50 mV s^{-1} using CV prior to the tests. The effective yielding area of the standard carbon electrode was 0.196 cm^2 . Table 2 lists the Pt loading of all samples used for CV.

2.3. Measurement of polarization curves

Membrane-electrode assembly (MEA) polarization curves were measured using a fuel cell workstation (Beam Associate Co., Ltd.). The Pt loading on both the anode and cathode was maintained at 0.4 mg cm^{-2} , and the effective area of the MEA was 5 cm^2 . A commercial hydrophobic carbon cloth (Beam Associate Co., Ltd.) was used as the gas diffusion layer. Nafion 112 (DuPont) membranes of an area of $4 \text{ cm} \times 4 \text{ cm}$, which was pretreated with 5 wt.-% H₂O₂ (Aldrich), deionized water, and $1.0 \text{ M H}_2\text{SO}_4$ solution (Aldrich, 98.5%) at 80 °C for 1 h, was used as the separator. Hydrogen and oxygen were provided to both the anode and cathode at a streaming rate of 100 sccm. The performance of the MEA was characterized at a potential sweep rate of 0.56 V min^{-1} at 25 and 75 °C using the fuel cell workstation. The humidifier temperature of both the anode and cathode was maintained at the same temperature as the MEA, and the polarization test was performed under ambient conditions.

3. Results and discussion

3.1. Characterization of the Pt/C catalyst

Fig. 1 shows the wide-angle XRD spectra of the Pt/C catalysts and the commercial 20 wt.-% Pt/C catalyst (JM-20 wt.-%-Pt/C). As can be seen in the figure, none of the diffraction peaks of CTAB appeared, implying that the CTAB was nearly removed from the synthesized

Table 1
The Pt loadings (wt.%) of the Pt/C catalysts by EDS and TGA.

Catalyst sample	Theoretical loading (wt.%)	The Pt loading (wt.%) by EDS	The Pt loading (wt.%) by TGA
Pt/C-4.12	20	18.76	19.02 ± 0.76
Pt/C-2.75	20	15.88	16.21 ± 0.72
Pt/C-1.37	20	11.36	11.12 ± 0.43

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