



Platinum catalysts protected by N-doped carbon for highly efficient and durable polymer-electrolyte membrane fuel cells



Hyeong Su Kim^a, Yeayeon Lee^a, Jin Goo Lee^b, Ho Jung Hwang^a, Jeongseok Jang^b, So Mi Juon^a, Altansukh Dorjgotov^b, Yong Gun Shul^{b,*}

^a Department of Graduate Program in New Energy and Battery Engineering, Yonsei University 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea

^b Department of Chemical and Bio-molecular Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul, 120-749, Republic of Korea

ARTICLE INFO

Article history:

Received 2 October 2015

Received in revised form 4 January 2016

Accepted 10 February 2016

Available online 12 February 2016

Keywords:

polymer-electrolyte membrane fuel cell

oxygen reduction reaction

nitrogen-doped carbon

catalyst

durability

ABSTRACT

Precious metals such as platinum are commonly used in polymer-electrolyte membrane fuel cells (PEMFCs) to enhance sluggish oxygen-reduction reactions. However, agglomerations of the nano-sized platinum and corrosions of the carbon supports degrade the performance and durability of the PEMFC during the long-term operation. Here, we present a highly active and durable catalyst for the oxygen-reduction reactions by covering carbon-supported platinum with nitrogen-doped carbons as a protective layer. The PEMFC with the NC-protected Pt/C cathode shows a power density of 1.06 W cm^{-2} at 0.6 V in $\text{H}_2\text{-O}_2$, comparable with 0.67 W cm^{-2} of the PEMFC with a commercial Pt/C cathode. Furthermore, the durability is remarkably enhanced over 50%, compared with the commercial carbon-supported platinum cathode. It suggests that the nitrogen-doped carbons as a protective layer are effective in enhancing the catalytic activity for oxygen-reduction reactions and durability of the PEMFCs.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered a promising energy conversion device in the future because of their high energy efficiency, low operation temperature, and low pollution emission. [1,2] Precious metals such as platinum (Pt) have been commonly used to enhance sluggish oxygen-reduction reactions (ORR). [2–4] However, serious deactivations of the catalysts due to agglomerations of the nano-sized Pt and corrosions of the carbon support appear during the long-term operation. [5,6] Recently, high-temperature PEMFCs (HT-PEMFCs) have been suggested for enhancement of the catalytic activity, tolerance of the CO poisoning, and simplification of the cooling systems, but the high-temperature operation accelerates the catalyst deactivations through the loss of electrochemically active surface area (ECSA) through the Ostwald ripening mechanism. [7] Thus, a number of researches have been focused on the development of highly active and durable catalysts for ORR. [8] Wang et al. reported the core-shell catalysts such as Au@Pt, Pt-decorated PdCo@Pd/C, and Pt@Co had significantly enhanced stability and ORR activity. [9–12] Additionally, the non-Pt catalysts such as nitrogen-doped carbon or alloy of precious metals such as

Ir, Pt, and Pd with transition metals such as Fe, Ni, or Co have been also reported. [13]

Pt nanoparticles have been typically dispersed on the carbon supports for the purpose of decreasing Pt loading in the fuel cell electrode. In particular, nitrogen-doped carbons (NC) are considered to serve as anchoring sites for metal nanoparticle deposition, concurrently promoting catalytic reactions. [14,15] However, the catalyst deactivations through the loss of the favorable electronic effect induced by the dissolution of transition metal still occur. To prevent the dissolution, Sakae et al. reported the Pt/CNT catalyst covered with hydrophobic silica layers. It improved the durability of the catalysts, but the catalytic activity depended on silica sources. Furthermore, when the catalysts were applied to the cathode of the PEMFCs, the cell performances were similar to or slightly lower than the cell with the commercial Pt/C. The NC has been studied for electrochemical catalysts, especially ORR, and several researchers showed that the NC is highly active for ORR. [16,17] At this point, if the NC with the high activity for ORR is used as a protective layer instead of the SiO_2 , the durability of the catalysts would be improved without decrease in the catalytic activity.

In this study, we report a novel Pt/C catalysts protected by NC layers to enhance both the catalytic activity for ORR and the durability of the PEMFCs. The Pt/C with 1 nm thickness of the NC annealed at 500°C showed the highest ORR activity and durability. Additionally, the PEMFCs with the catalysts as a cathode showed

* Corresponding author

E-mail address: shulyg@yonsei.ac.kr (Y.G. Shul).

approximately 1788 mA cm^{-2} at 75°C (relative humidity: 100%) and 389 mA cm^{-2} at 120°C (relative humidity: 40%) at 0.6 V, which is superior to that of the PEMFCs with the commercial Pt/C. The cell durability was also enhanced with a degradation rate of only 11.97% (commercial Pt/C: 23.16%) in low-temperature PEMFCs. The enhancement of the cell durability appeared in high-temperature PEMFC tests. Hence, when the active NC layers for ORR are covered around the Pt nano-particles and carbon supports as a protective layer, the PEMFCs would obtain not only the improved performances but also the enhanced durability.

2. Experimental procedures

2.1. NC/Pt/C catalysts

The commercial 20% Pt/C (HISPEC 3000, A Johnson Matthey company, 0.1 g) and Ethylenediamine (99%, Duksan pure chemical co. $67 \mu\text{L}$ for 1 nm thickness of the NC and $200 \mu\text{L}$ for 3 nm thickness of the NC) were placed in distilled water of 100 mL. The suspension was refluxed with stirring at 75°C for 8 h. The suspension was washed and filtered with distilled water and ethanol, and then dried in oven at 60°C for 8 h. The catalysts were annealed at different temperatures from 400°C to 700°C in Ar for 2 h.

2.2. Physical properties of the catalysts

The 1 nm- and 3 nm-thick NC/Pt/C annealed at different temperatures were measured by using high resolution transmission electron microscopy (HR-TEM, JEOL/JEM-ARM 200 F model) to define the NC layers around the Pt nano-particles and carbon supports. Crystallite sizes of the NC/Pt/C samples were obtained from X-ray diffractometer (XRD, Rigaku D/MAX-2500) with a $\text{Cu K}\alpha$ ($\lambda = 1.541 \text{ \AA}$) at 40 kV. The N species were analyzed by using FT-IR (Bruker/Vertex70), CHNS (Perkin Almer Co. Ltd./2400 series II CHNS/O), and X-ray photoelectron spectroscopy (XPS, Thermo U. K./K-alpha).

2.3. Performances of the NC/Pt/C catalysts in half-cell tests

The catalytic activities of the NC/Pt/C samples were measured by using three-electrode system with rotation disk electrode (RDE) through linear sweep voltammetry (LSV). The RDE with 10 mm outer diameter and 5 mm inner diameter was used as a working electrode, and the rotator (Pine, AFMSRCE model) was used. Pt mesh and saturated calomel electrode (SCE) were used as a counter and reference electrode, respectively. The catalysts (30 mg) and Nafion solution (5%, $60 \mu\text{L}$) were dispersed in 1.2 mL distilled water/ethanol (1:10 vol.) with sonication. The slurry was dropped on the glassy carbon electrode with Pt loading of $2.8 \mu\text{g cm}^{-2}$. The LSV was taken in 0.5 M H_2SO_4 , on rotating disc electrode at a rotating speed of 1600 rpm and at a scan rate of 10 mV s^{-1} . The catalytic durability of the NC/Pt/C samples was measured by using three-electrode system with rotation disk electrode (RDE) through cyclic voltammetry (CV). The slurry was dropped on the glassy carbon electrode with Pt loading of $2.1 \mu\text{g cm}^{-2}$. The CV (200 cycles) was taken in 0.5 M H_2SO_4 , on rotating disc electrode at a rotating speed of 1600 rpm and at a scan rate of 50 mV s^{-1} (voltage sweep: from -0.2 V to 1.35 V).

2.4. Slurries of the NC/Pt/C in the PEMFCs

The commercial 40% Pt/C (HISPEC 3000, A Johnson Matthey Company) and NC/Pt/C catalysts were used as an anode and cathode, respectively. The catalyst slurries were fabricated by dispersing the catalysts in Aquivion solution (15 wt. % solution in

aliphatic alcohol/ H_2O mixture, EW=870, Solvay Solexis) and isopropyl alcohol.

2.5. MEA fabrications

Membrane electrode assembly (MEA) was fabricated by catalyst coated membrane (CCM) method. $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ as an anode and $0.2 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ as a cathode were sprayed on the Aquibion membrane (Solvey solexis, E87-05S, $50 \mu\text{L}$) by using spray gun. The membrane with a short side chain perfluorosulfonic acid group is known to show the stability at high temperature of 120°C and low relative humidity conditions. Gas diffusion layer (GDL) used carbon papers (SIGRACET, GDL-10BC, thickness = $415 \pm 55 \mu\text{m}$, Germany).

2.6. Performances of the NC/Pt/C catalysts in the PEMFCs

Performances of the PEMFCs were evaluated by using the fuel cell measurement system (BekkTech, USA) with DC electronic load (6060B, Hewlett Packard). The I-V curves were obtained in a voltage range from 0.05 V to 1.05 V with 0.05 V intervals. The flow rates of H_2 and O_2 were 100 mL min^{-1} and 150 mL min^{-1} , respectively. The cell tests were carried out at 75°C (relative humidity: 100%) and at 120°C (relative humidity: 40%), respectively. Electrochemical properties were measured by electrochemical analyzer (Bio-logic, France) and AC impedance spectroscopy (Bio-logic). The CV was conducted through the potential sweep from 0.05 V to 1.2 V at 50 mV s^{-1} , purging N_2 gas into the cathode side.

2.7. Durability of the NC/Pt/C catalysts in the PEMFCs

The accelerated life-time (ALT) tests were carried out at 120°C (relative humidity: 40%) due to fast degradation rate of the PEMFCs at high temperatures. [1–3] The ALT protocol was indicated in Fig. S1. The ALT tests had the potential sweep from 0.6 V to 1.0 V with 0.05 V intervals, and the current density was detected, remaining each voltage step for 15 s. It takes about 4.25 min for 1 cycle, and total cycles were 510 cycles (36 h). The CV cycling tests were carried out through the potential sweep from 0.6 V to 1.0 V at 50 mV s^{-1} , purging N_2 gas into the cathode side.

3. Results and discussion

3.1. NC thickness effects

Fig. 1 shows the TEM images of the NC/Pt/C annealed at 500°C . Dark gray layers were covered around carbon supports and Pt nano-particles, and the layer thicknesses were approximately 1 nm and 3 nm, respectively (Fig. 1a and 1b). The NC/Pt/C structures had the uniformity in this study (Fig. S2). The FT-IR spectra clearly shows that the Pt/C catalysts were covered with the NC layers, indicating 2350 cm^{-1} as C=N nitrile group and $2850\text{--}3000 \text{ cm}^{-1}$ as C-H vibration (asymmetric/symmetric) (Fig. S3). [18] The crystallite sizes of the Pt nano-particles were calculated from the XRD patterns of the commercial and NC/Pt/C catalysts depending on annealing temperatures by using Scherrer equation (Fig. S4). [19] The crystallite sizes were approximately 3.3, 5.7, 6.6, 7.7, and 9.4 nm in the commercial and NC/Pt/C annealed at 400, 500, 600, and 700°C , respectively. It reveals that regardless of the NC thickness, the crystallite size of the Pt nano-particles depend on the annealing temperatures. To investigate the effects of the NC thickness on the catalytic activity for ORR, linear sweep voltammetry (LSV) was measured by using rotating disk electrode (RDE) in O_2 -saturated 0.5 M H_2SO_4 solution at scan rate of 10 mV and rotating speed of 1600 rpm. Despite the larger crystallite size

Download English Version:

<https://daneshyari.com/en/article/183217>

Download Persian Version:

<https://daneshyari.com/article/183217>

[Daneshyari.com](https://daneshyari.com)