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Enhanced oxygen reduction reaction of Pt deposited Fe/N-doped bimodal porous carbon nanostructure catalysts

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ABSTRACT

For commercialization of proton exchange membrane fuel cells (PEMFCs), the loading amount of Pt-based cathode catalysts for oxygen reduction reaction (ORR) needs be significantly reduced. In this study, we propose Pt catalysts supported by an iron/nitrogen-doped porous carbon (FeNC) nanostructure having a catalytic activity for ORR in order to significantly reduce the utilization of Pt. The FeNC nanostructure was prepared using a template method with 50 and 500 nm SiO_2 beads and phthalocyanine as a dopant and carbon source. The nanosized Pt catalysts with different loading weights (5, 10, 20, 30 wt%) were uniformly deposited on the FeNC with a bimodal porous crystalline doped carbon nanostructure using an electron beam radiation method. In particular, the cathode catalyst having 5 wt% Pt on FeNC (Pt5/FeNC) exhibited enhanced ORR mass activities of 2.19 and 2.58 A mg_{Pt}^{-1} at 0.9 V measured by electrochemical half cells in acidic and alkaline media, respectively, compared to a commercial Pt(20 wt%)/C (Pt20/C). Furthermore, Pt5/FeNC showed a higher mass activity of 18.76 A mg_{Pt}^{-1} at 0.6 V as a unit cell performance than that of the commercial catalyst. The improved ORR activity of Pt/FeNC might be synergistically attributed to the homogeneous dispersion of Pt nanoparticles on the bimodal porous doped carbon nanostructure, the interaction (electronic effect) between the metallic catalyst and the doped support, and the dual catalytic effect of both Pt and the doped carbon nanostructure.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are electrochemical power generating systems, that can directly convert chemical energy into electricity at a relatively low temperature (~80 °C) [1–4]. In PEMFCs, protons and electrons are generated by the oxidation of hydrogen as a fuel at the anode and by the reduction of oxygen at the cathode, producing electricity and water as a by-product [5]. The oxidation and reduction at the anode and cathode, respectively, in PEMFCs are mainly based on electrocatalysis on precious metal (Pt, Pd, and Ir) catalysts [5–7]. In particular, slow oxygen reduction reaction (ORR) at the cathode, compared to hydrogen oxidation reaction at the anode, is responsible for the high loading amount of Pt-based cathode catalysts in PEMFCs [8]. Accordingly, much effort has been made to reduce the utilization of precious metal cathode catalysts and/or improve the utilization of the catalyst [9]. To reduce the loading amount of precious metal catalysts at the cathode, intensive studies have been carried out on the size-control of the precious metals for an increased active surface area, alloy formation between precious and non-precious metals, and the synthesis of catalyst nanoparticles (NPs) deposited on various supporting materials [5,9–14].

In particular, the support materials in the supported catalysts need to have excellent electrical conductivity, a high specific surface area, chemical stability, and a porous structure [15–18]. The structure and surface properties of the support could affect the dispersion, particle size, and stability of the catalyst on the support [5,19,20]. Recently, non-precious metal (NPM) catalysts such as doped carbon nanostructures having an electrocatalytic activity for the ORR have been utilized as a support to reduce the loading amount of precious metal catalysts [10,21–23]. Carbon nanostructures doped with heteroatoms (Fe, Co, N, B, and S) exhibited

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enhanced ORR performance comparable to a commercial Pt catalyst [24–28]. Transition metal/nitrogen-doped carbon structures have been intensively studied due to their highly electrocatalytic active sites for improved ORR activity [29–31]. Transition metal/nitrogen-doped carbon nanostructures have been utilized as a support with an electrocatalytic activity to deposit Pt nanoparticles (NPs) [32–37]. Zhou et al. reported that the use of nitrogen as a dopant in the carbon support could induce the interaction between the Pt NPs as a catalyst and the doped carbon as a support, enhancing the dispersion of Pt NPs and catalytic properties [21,23]. Thus, the N-doped carbon nanostructure supports having an electrocatalytic activity are expected to improve the ORR activity and thus reduce the utilization of Pt NPs.

In this study, we prepared a doped porous carbon nanostructure with an electrocatalytic activity for ORR using a silicate template method with iron phthalocyanine as the doping and carbon sources. We then deposited Pt NPs on the doped carbon support. The samples were characterized using field-emission transmission electron microscopy (FE-TEM), field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The specific surface areas of the samples were analyzed using nitrogen adsorption/desorption isotherms. The electrochemical properties of the samples were measured using cyclic voltammetry and linear sweep voltammetry in a typical electrochemical cell. The performance of the H_2/O_2 PEMFCs using the samples as cathode catalysts was evaluated using a unit cell measurement.

2. Experimental

2.1. Synthesis of the doped carbon support

To synthesize doped porous carbon nanostructures as supports, 3 g iron phthalocyanine (Fe-Pc, Aldrich) was dissolved in 100 mL dimethylformamide (DMF, Aldrich) and then mixed with 3 g 500 nm silicate beads (Alfa Aesar) and 3.33 g 50 nm silicate beads (30% in ethylene glycol, Alfa Aesar). The mixed solution was transferred in a glass petri dish to an oven and dried at 80 °C for 12 h. The dried powder was heated at 900 °C for 3 h in an N_2 atmosphere [29,31,38–40]. The heated sample was stirred in 10% hydrogen fluoride (HF) solution for 5 h to completely remove the silicate template and impurities, and was then washed with de-ionized (DI) water several times. The resulting powder for used in the support was obtained by drying in a 50 °C oven for 24 h. To identify the doping effect of the support, the undoped carbon nanostructure (UDC) was prepared by the same procedure as that used for the doped nanostructure, with poly(furfuryl) alcohol (PFFA, Polysciences) as a carbon source (instead of Fe-Pc) and acetone as a solvent (instead of DMF). To confirm the Fe-doping effect of the support, the N-doped carbon nanostructure (NC) was prepared by the same procedure as that used for the doped nanostructure, with Pc as a nitrogen and carbon source and DMF as a solvent.

2.2. Synthesis of supported Pt catalysts

The supported catalysts with different weight ratios of Pt NPs were prepared with the doped/non-doped porous carbon nanostructures and Vulcan XC-72R using an electron beam radiation method. A Pt precursor (H_2PtCl_6, Aldrich) was dissolved in DI water and mixed with the corresponding support. The Pt ions were reduced to Pt atoms by electron beam radiation with an accelerating voltage and current of 0.2 MeV and 5 mA, respectively, for 20 min. The Pt NPs were formed by aggregation of Pt atoms and simultaneously deposited on the support.

2.3. Materials characterization

The crystal structure of the samples was performed using XRD analysis (Bruker, D2 Phase System) with a Cu K_α ($\lambda = 0.15406$ nm) radiation, a tube voltage of 30 kV, and current of 10 mA. The morphology of the samples was confirmed using FE-SEM (JSM-7001F) operating at 15 kV. The structure and dispersion of the samples were observed using FE-TEM (JEM-ARM 200F) operating at 200 kV. For the TEM analysis, the samples dispersed in ethanol were dropped on carbon-free Cu grids. The elemental composition and chemical states were characterized using XPS analysis (Thermo Scientific, K-Alpha) with Al K_α ($\lambda = 1486.8$ eV) source and beam power of 200 W under a chamber pressure of 2.9×10^{-8} Torr. The specific surface area and pore structure of the samples were analyzed through nitrogen gas adsorption-desorption isotherms (Micromeritics ASAP 2020 adsorption analyzer).

2.4. Electrochemical analysis

The electrochemical properties of the samples were analyzed using a potentiostat (Eco Chemie, AUTOLAB) in a three-electrode electrochemical cell at 25 °C. The catalyst inks were prepared by homogeneously mixing the samples with DI water, isopropanol (Aldrich), and Nafion® ionomer (5 wt%, Aldrich). The ink was dropped on a polished glassy carbon electrode and dried in a 50 °C oven for 10 min. The resulting amount of catalyst deposited on the glassy carbon electrode as a working electrode was ~200 μg cm^{-2}. Pt wire and Ag/AgCl (in 3 M KCl) were used as counter and reference electrodes, respectively. Cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) of the samples were obtained in 0.1 M $HClO_4$. A stability test of the catalysts for the ORR was conducted by sweeping between 0.4 and 0.9 V (vs. Ag/AgCl) for 10,000 cycles in O_2-saturated 0.1 M $HClO_4$ or 0.1 M NaOH with a scan rate of 50 mV s^{-1}.

To prepare the membrane electrode assembly (MEA), a decal method was used with the as-prepared samples as cathode catalysts. The catalyst ink was prepared by mixing 0.15 g catalyst with DI water, isopropyl alcohol (IPA), and 5 wt% Nafion solution. The ink was coated on a Teflon film using ultrasonic spraying and transferred to a pre-treated Nafion membrane (211, DuPont) by hot-pressing at 120 °C under 40 bar for 2 min. The total weight of the cathode catalyst with a content of 30 wt% Nafion was ~3 mg cm^{-2}. The electrode deposited with Pt(20 wt%)/C on carbon paper (~0.5 mg_{Pt} cm^{-2}) was used as an anode. The MEA was fabricated with the anode, membrane, and cathode by hot-pressing at 120 °C under 40 bar for 2 min. The fabricated MEA was inserted between graphite plates with a serpentine flow-field (active area ~5 cm^2) and metal plates as current collectors. It was then assembled for a single cell measurement. The performance of H_2/O_2 PEMFC using the fabricated MEA was evaluated at 80 °C under an ambient pressure using a computer-controlled electronic load (CNLPEM005-01, CNL Energy Co.). The hydrogen and oxygen humidified at 65 °C were supplied with flow rates of 100 and 300 mL min^{-1}, respectively.

3. Results and discussion

3.1. Structural characterization of catalysts

The samples used as supports were prepared by the template method using silicate beads with diameters of 500 and 50 nm and Fe-Pc as both carbon and doping sources and pyrolysis at 900 °C under an N_2 atmosphere. As shown in Fig. 1(a) and (b), the as-prepared sample exhibited a porous nanostructure with meso- and macro-pores of ~50 and ~500 nm, in diameter,