



Research Paper

Soft-template synthesis of mesoporous non-precious metal catalyst with Fe-N_x/C active sites for oxygen reduction reaction in fuel cells

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ABSTRACT

We synthesized ordered mesoporous Fe/N/C with highly active Fe-N_x/C sites denoted as m-FePhen-C as a non-precious metal catalyst (NPMC) for the oxygen reduction reaction in fuel cells. This was the first study that incorporated a catalyst precursor with Fe-N coordination directly in a simple block co-polymer-assisted soft-template method for the synthesis of mesoporous Fe/N/C. The synthesized catalyst (m-FePhen-C) showed a high catalytic performance comparable to that of Pt/C in half-cell tests, and a membrane electrode assembly (MEA) with an m-FePhen-C cathode exhibited 40% higher power density than did an MEA with a commercial Pt/C cathode in single-cell tests, with comparable electrode thicknesses. This result is highly meaningful in that generation of the Fe-N_x/C active sites and formation of ordered mesoporous structure were achieved simultaneously in the simple soft-template-assisted process, and in that the advantages of mesoporous structure with appropriate pore size in metal-containing NPMC were elucidated for high-performance MEAs.

1. Introduction

A fuel cell that uses a polymer electrolyte and operates at low temperature is a promising substitute for a conventional power generator in vehicles, owing to its high energy conversion efficiency and ecologically benign products [1–3]. The oxygen reduction reaction (ORR) occurring at the cathode of a fuel cell has slow kinetics, and therefore limits the performance of the fuel cell. The most common catalyst to accelerate the ORR is platinum nanoparticles supported on carbon (Pt/C). However, the high cost of Pt impedes the widespread application of fuel cells. Although the use of Pt-alloy catalysts has been considered as an alternative strategy to increase the ORR activity with less Pt [4–6], it is not a permanent solution, as Pt is scarce.

For the complete replacement of Pt in the cathode, non-precious metal catalysts (NPMCs) have recently been studied [7–9]. In this regard, anion exchange membrane fuel cells (AEMFCs) also have been highlighted, because the ORR on NPMCs tends to be faster in alkaline conditions than acidic conditions [2,3]. Covalent doping with heteroatoms is a common method to achieve ORR activity using carbon materials. Changes in the charge and spin densities of carbon atoms have been considered as the origin of the ORR activity of the heteroatom-doped carbon materials [10–13]. Meanwhile, incorporating metal in heteroatom-doped carbon leads to greater enhancement of the ORR activity. Since Jasinski's work [14], composites of nitrogen-doped carbon-based materials and third-row transition metals (i.e., Fe or Co) have been developed as ORR catalysts [7,15,16]. In particular, iron-

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containing nitrogen-doped carbons (Fe/N/Cs) have shown outstanding ORR activity. Fe/N/C is generally synthesized by pyrolyzing a mixture of Fe, N, and C precursors at a high temperature ($> 800\text{ }^{\circ}\text{C}$) in an inert atmosphere [8,9,17].

The generation of active catalytic sites is important for the development of NPMCs. The Fe-N_x/C site, at which a single Fe ion is coordinated to N functionalities at the edge of a carbon basal plane, is a molecule-type active site that is considered as the main active site for ORR in Fe/N/C [18–21]. The Fe-N_x/C site accelerates the ORR significantly under alkaline conditions. The key factors for the ORR occurring at the Fe-N_x/C site are the Fe³⁺/Fe²⁺ transition potential and stabilization of the peroxide intermediate. In alkaline conditions (pH > 12), the transition of Fe³⁺ to Fe²⁺ occurs at high potential and the anionic peroxide intermediate (HO₂⁻) is strongly stabilized on the Fe-N_x/C site; therefore, the overpotential of ORR is reduced and a desirable 4e⁻ ORR pathway is highly preferred [18,22]. However, because the catalyst that contains the Fe-N_x/C site is synthesized by heat-treatment of a precursor mixture containing Fe, N, and C at a high temperature ($> 800\text{ }^{\circ}\text{C}$), at which the Fe-N_x/C site is not stable, the development of a controlled synthesis is required to dominantly generate the Fe-N_x/C site in the catalyst [22–25]. An intuitive way to generate the site is to use precursors that are analogous to the Fe-N_x/C site, where an Fe ion is coordinated to nitrogen functionalities in aromatic rings (Fe-CNAR precursor) [7,15,17]. Even if the molecular structure of the precursor is changed significantly during the high-temperature pyrolysis, this approach can be expected to generate more Fe-N_x/C molecule-type catalytic sites than using a simple mixture of the Fe, N, and C precursors with no coordination.

To practically utilize an NPMC with Fe-N_x/C active sites in the cathode of the fuel cell, the accessibility of the active site should be considered carefully. Fuel cell cathodes made of carbon-based NPMCs usually have high mass-transport resistance, because most of the active sites are buried inside the catalyst particles, and because the catalyst layer is relatively thick owing to the low volumetric activity of the NPMC [15]. The high mass-transport resistance, which is exerted on the reactants as they approach the catalytic sites, reduces the reaction kinetics and makes the utilization of active sites inefficient. This feature appears distinctly in a single-cell performance test performed using a membrane electrode assembly (MEA) [26–28]. Many cathodes made of NPMCs have exhibited much lower performances than that of Pt/C in a single-cell system, even if the NPMCs showed comparable or superior ORR kinetic activities to Pt/C in half-cell tests with a rotating-disk electrode (RDE) [28]. Although there have been a few reports of MEAs with NPMC cathodes exhibiting higher performance than MEAs with Pt/C cathodes, in the case of fuel cells using alcohols as the fuel fed into the anode, the current densities and power densities are too low [29–31]. To minimize the mass-transport resistance of an NPMC and to enable the catalyst to exhibit the best performance in a practical fuel cell system, the nanoporosity of the NPMC must be controlled.

An ordered mesoporous structure can provide both high surface area and facile mass transport in pores [32–34], and is therefore highly desirable in practical NPMCs [15,28,35]. The hard-template method is a common strategy to synthesize mesoporous materials with a negative-replica structure of a porous template (e.g., mesoporous silica) [36–40]. However, the synthesis process is time-consuming and involves tedious steps because of the required formation and removal of the template material. Meanwhile, soft-template synthesis is a simple and useful alternative to fabricate a mesoporous material. This method requires very simple steps, including the assembly of a structure-directing agent (SDA) and precursors of target materials, and subsequent pyrolysis [41–43]. Unfortunately, the self-assembly of the SDA is sensitive to the interaction of the assembly agents; therefore, the direct incorporation of the precursor to form the Fe-N_x/C sites has been difficult. It is highly desirable to develop a soft-template synthesis for a mesoporous NPMC with Fe-N_x/C sites by incorporating Fe-CNAR precursors during the self-assembly step. In addition to the high kinetic activity and mass

transport of the catalyst, simplicity of the synthesis can be achieved.

Herein, we report a simple soft-template process to synthesize an ordered mesoporous NPMC with Fe-N_x/C active sites (m-FePhen-C) by the direct incorporation of an Fe-CNAR precursor (complex of Fe²⁺ ion and 1,10-phenanthroline (phen)) in the block co-polymer self-assembly. Compared to previous works that involved impregnating a preformed mesoporous template with catalytic site precursors, heating the composite, and removing the template to make mesoporous Fe/N/C, the synthesis reported in this work is much simpler, in that the active sites and ordered mesoporous structure are formed simultaneously in a single step [15,16,35]. Moreover, this is notably the first report of an Fe-CNAR precursor being directly incorporated in a block co-polymer-assisted soft-template method for the synthesis of mesoporous Fe/N/C. Many reports about NPMCs have reported only the kinetic activities of catalysts measured in the half-cell system, even though the catalytic performance in a practical single-cell system can be totally different from that in a half-cell system. Desirably, m-FePhen-C showed high catalytic performance both in half-cell and single-cell systems [28]. The kinetic activity measured in the half-cell system was higher than that of Pt/C, and an MEA with an m-FePhen-C cathode showed 40% higher power density than did an MEA with a commercial Pt/C cathode in single-cell performance tests, in which the catalyst loadings and electrode thicknesses were comparable.

2. Experimental

2.1. Synthesis of m-FePhen-C

Pluronic F127 (Aldrich) 0.64 g was dissolved in a co-solvent of ethanol (2.23 mL) and 0.2 M HCl (0.22 mL). The Fe(phen)₃Cl₂ complex was prepared separately by mixing FeCl₂·4H₂O (93 mg) and 1,10-phenanthroline (253 mg) in the co-solvent of ethanol (16.9 mL) and 0.2 M HCl (1.67 mL). Resol (0.26 g) [44], tetraethylorthosilicate (TEOS) (Aldrich, 0.892 mL), and the Fe(phen)₃Cl₂ complex solution (7 g) were added to the polymer solution. After being stirred for 1 h, the solution was poured to a dish. The solvent was evaporated at 50 °C, and the dish was stored in an oven at 100 °C for 24 h. The obtained polymeric nanocomposite was pyrolyzed at 900 °C for 2 h (ramping rate: 1 °C min⁻¹ to 350 °C; 350 °C was maintained for 3 h; 1 °C min⁻¹ to 600 °C; 5 °C min⁻¹ to 900 °C). Decomposition of F127 occurs severely around 350 °C, and polymeric phenolic resin (obtained by polymerization of resol) is converted to a conductive carbon structure or is partly decomposed below 600 °C [42,45]. To make such intense changes take place slowly and not affect to the catalyst structure, we increased the temperature slowly (1 °C min⁻¹) below 600 °C. Keeping the temperature at 350 °C for 3 h was for the complete decomposition of F127. Above 600 °C, the structure of carbon crystallite is changed [45]. Because this change is less intense than the changes occurring below 600 °C, this change is less likely to affect the catalyst structure. Therefore, we increased the temperature fast above 600 °C (5 °C min⁻¹). Silica in the framework was removed by etching in 10 wt. % HF solution (25 °C, 2 h). m-FePhen-C was finally obtained by the second heat-treatment at 900 °C in Ar for 1 h (ramping rate: 3 °C min⁻¹). The second heat-treatment was required to remove the anions or impurities that could bind to the active sites during the etching process [46]. Even if the removal of anion or impurities is not an intense change that affects the structure of the catalyst, the water or oxygen molecules adsorbed on the catalyst surface can damage the catalytic site during the heat-treatment when the sample is heated too fast from room temperature to 900 °C. Therefore, we used an intermediate ramping rate of 3 °C min⁻¹ in the second heat-treatment.

2.2. Synthesis of sample set for comparison of electrochemical catalytic activity

b-FePhen-C was synthesized by the same procedure as that of the

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