Oxygen Reduction Catalytic Activity of Carbon-based Cathode Catalyst Prepared from Polyimide Nanoparticles Containing Fe-Phenanthroline Complex

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1. Introduction

Electrochemical oxygen reduction reaction (ORR) in acidic media is a very important reaction since it has attractive applications such as proton exchange membrane fuel cells (PEMFCs). For the globalization of PEMFCs, much efforts are being made to reduce the amount of Pt in the cathode. Especially, the development of the non-precious-metal (NPM) catalysts for ORR is strongly desired [1]. Since Jasinski discovered the catalytic activity of cobalt phthalocyanine [2] for ORR and Jahnke et al. reported the heat treatment of cobalt dibenzotetraazaannulene (CoTAA) [3], numerous attempts have been made to develop NPM cathode catalysts by the pyrolysis of precursors that contain transition metals (mainly Fe or Co), a nitrogen source, and a carbon source [4-10].

Our research group has been developing NPM cathode catalysts prepared by the pyrolysis of spherical polyimide fine particles with a small amount of Fe additive. We have already reported that many nitrogen containing polymers, such as polyimides and polyamides, can be converted into catalytically active carbon materials by pyrolysis at high temperatures [11]. In addition, the morphology of polyimide can be controlled through precipitation polymerization, and the fine particle morphology can be retained after carbonization [8]. To date, such a polyimide-derived NPM catalyst is a state-of-the-art NPM cathode catalyst, showing a quite promising fuel cell performance under a 0.2 MPa air atmosphere at 80 °C: 1.0 A cm⁻² at 0.46 V, owing to the oxygen diffusion enhanced by the well-controlled morphology [10].

The objective of this study is to further optimize the synthesis method of the polyimide nanoparticles. Scheme 1 shows our conventional synthetic route for polyimide nano-particles. Polyimide nano-particles can be synthesized via precipitation polymerization. At this polymerization stage, Fe(acac)₃, which is necessary for ORR catalytic activity, is added as an Fe source. Since this polyimide does not have coordination capability to Fe cations, the Fe species are not well mixed or immobilized with the polyimide in a molecular level. Indeed, if one filter the polymerization slurry, the majority of Fe species is extracted into the filtrate rather than remaining in the residue (Figure 1). In our previous study, therefore, the solvent for the polymerization was removed by evaporation to guarantee the Fe content in the resulting powder. This works quite well in a flask scale but might suffer from ununiformity in the scaled up reactions for commercialization. In contrast, the current study focuses on the copolymerization of Fe complex and the monomers for polyimide as shown in Scheme 2. 5-Amino-1,10-phenanthroline (amph) is utilized as a ligand to immobilize the Fe cations and their complex, Fe(amph)₃(ClO₄)₂, is investigated as a co-monomer for the precipitation polymerization. The results of carbonization and electrochemical measurements are discussed in terms of the comparison between the conventional method with Fe(acac)₃ and the current one with Fe(amph)₃(ClO₄)₂.

2. Experimental

2.1. Materials
Pyromellitic acid dianhydride (PMDA) was purified by sublimation before use. Fe(amph)$_3$(ClO$_4$)$_2$·2H$_2$O was prepared from FeCl$_2$ and amph by a literature method [12]. Other chemicals were used as purchased unless otherwise stated.

2.2. Synthesis of Fe(acac)$_3$/PI

A solution of TAPB (1.41 g, 4 mmol) in acetone (45 mL) was added to a solution of PMDA (1.31 g, 6 mmol), Fe(acac)$_3$ (54.3 mg, 0.15 mmol) and N,N-dimethyldodecylamine (DMDA, 0.3 mL) in acetone. The mixture was vigorously stirred for 30 min at 0 °C. After evaporating the solvent, the curing reaction proceeded by heating the poly(amic acid) at 240 °C under evacuation to obtain polyimide nanoparticles, Fe(acac)$_3$/PI.

2.3. Synthesis of Fe(amph)$_3$/PI

A solution of Fe(amph)$_3$(ClO$_4$)$_2$·2H$_2$O (116 mg, 0.13 mmol) in acetophenone (30 mL) was added to a solution of PMDA (1.31 g, 6 mmol) in acetophenone (50 mL). The mixture was stirred for 10 min at 25 °C, and then DMDA (0.19 mL) was added. After 15 min of stirring, a solution of TAPB (1.36 g, 3.87 mmol) in acetophenone (20 mL) was added, and then the mixture was vigorously stirred for 1 h at 25 °C. After evaporating the solvent, the curing reaction proceeded by heating the poly(amic acid) at 240 °C under evacuation to obtain polyimide nanoparticles, Fe(amph)$_3$/PI.

2.4. Carbonization

Fe(acac)$_3$/PI and Fe(amph)$_3$ were pyrolyzed in the following manner to obtain Fe(acac)$_3$/PI-1000-NH$_3$ and Fe(amph)$_3$/PI-1000-NH$_3$, respectively. The Fe-containing polyimide precursor was heated at 600 °C for 5 h in a nitrogen atmosphere, and then heated again to 800 and 1000 °C for 1 h each in an ammonia atmosphere (50% balanced by nitrogen). PI-800-NH$_3$ without any Fe additive was also prepared from Fe-free polyimide nano-particles, but the heat treatment at 1000 °C was omitted because the Fe-free polyimide does not leave any carbonaceous residue under such an atmosphere. This is because the catalysis by Fe clusters are important to enhance carbonization [13].

2.5. Measurements

The characterization of the prepared samples was carried out by N$_2$ adsorption, CHN elemental analysis, electron probe micro analysis (EPMA), field emission scanning electron microscopy (FE-SEM) and rotating rind-disk electrode voltammetry (RRDE). The details for these measurements are described elsewhere. [8]
3. Results and discussion

3.1. Precipitation polymerization

Scheme 1 shows the synthetic route to obtain Fe(acac)$_3$/PI. When the polymerization slurry is filtered, the majority of Fe species is extracted into the filtrate rather than remaining in the residue (Fig. 1a and 1c). Fig. 2a shows an FE-SEM image of Fe(acac)$_3$/PI. Quite fine polyimide particles can be observed, as previously reported [10].

Scheme 2 shows our new method to incorporate the Fe additive into the polymer chains. Acetophenone was employed as the solvent because Fe(amph)$_3$(ClO$_4$)$_2$·2H$_2$O does not dissolve in acetone, and the reaction temperature was raised to 25 °C because of high viscosity of acetophenone at a lower temperature. The concentration of DMDA, which is a dispersant to make fine and uniform particles, was optimized as 0.15 wt% for these monomers and solvent. Fig. 2b and 2d show the photo images of the dark-colored residue and the transparent filtrate from the polymerization slurry in Scheme 2. This observation suggests that the Fe cations are successfully incorporated into the polyimide main chains. Fig. 2b shows a FE-SEM image of Fe(amph)$_3$/PI. Although the particle size seems slightly larger than that of Fe(acac)$_3$/PI, numerous particles can be observed.

3.2. Carbonization

The filtration was conducted to confirm the incorporation of Fe species by observing the color difference. The actual solvent removal in the precursor synthesis for real catalysts was done by evaporation, and the obtained samples were carbonized by the heat treatment.

Fig. 3a and 3b respectively show the FE-SEM images of Fe(acac)$_3$/PI-1000-NH$_3$ and Fe(amph)$_3$/PI-1000-NH$_3$ after the carbonization. Spherical carbon particles can be observed in Fig 3a. The particle shape in Fig. 3b seems slightly distorted, but still retains the fine structure.

Table 1 and 2 show the results of characterization for the carbonized samples. Fe(acac)$_3$/PI-1000-NH$_3$ and Fe(amph)$_3$/PI-1000-NH$_3$ show similar
properties in terms of chemical compositions and specific surface area. The Fe-free sample shows a higher nitrogen content and a lower specific surface area because it was treated at lower temperature without the catalysis by Fe species for carbonization.

Fig. 4. RRDE voltammograms with the prepared cathode catalysts. Temperature: RT, catalyst loading: 0.2 mg cm\(^{-2}\), electrolyte: 0.5 M H\(_2\)SO\(_4\) (O\(_2\) saturated), rotation: 1500 rpm. Upper panel: selectivity to H\(_2\)O\(_2\), lower panel: ORR current density.

3.3. ORR catalytic activity

Fig. 4 shows the RRDE voltamograms with the carbonized samples. Fe-free sample, PI-800-NH\(_3\) shows poor ORR current and the selectivity to H\(_2\)O\(_2\) is quite high. This is probably because the Fe-free nitrogen-doped carbon has only the catalytic activity for two electron reduction to H\(_2\)O\(_2\) in acidic media [14,15]. In contrast, both of Fe(acac)\(_3\)/PI-1000-NH\(_3\) and Fe(amph)\(_3\)/PI-1000-NH\(_3\) show higher ORR current with lower selectivity to H\(_2\)O\(_2\). Probably, some Fe containing active sites are responsible to further reduce H\(_2\)O\(_2\) to H\(_2\)O, resulting a quasi-four electron reduction. [14-16] The ORR catalytic performances were similar between these two samples, suggesting that the Fe species introduced by the copolymerization work as well as those from Fe(acac)\(_3\).

4. Conclusion

Copolymerization of PMDA, TAPB and Fe(amph)\(_3\)(ClO\(_4\))\(_2\) has been studied as a synthesis method to prepare Fe containing polyimide nanoparticles. The obtained polymer can be converted into a NPM cathode catalyst by carbonization. The resulting carbon-based catalyst exhibits as good ORR performance as a state-of-the-art NPM catalyst. The current method will be suitable for a scaled up process since the incorporation of Fe species into the polymer chains will contribute to uniform dispersion of Fe source.

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References