

## Non-Precious-Metal Fuel Cell Catalyst Prepared from Fe Containing Polyimide Nano-Particles

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**Abstract:** The development of a non-precious metal (NPM) fuel cell catalyst is extremely important to achieve globalization of polymer electrolyte fuel cells due to the cost and scarcity of platinum. Here, we report on a NPM cathode catalyst prepared by the pyrolysis of spherical polyimide nanoparticles that contain small amounts of Fe additive. 60 nm diameter Fe-containing polyimide nanoparticles were successfully synthesized by the precipitation polymerization of pyromellitic acid dianhydride and 1,3,5-tris(4-aminophenyl)benzene with Fe(acac)<sub>3</sub> (acac = acetylacetonate) as an additive. The particles were subsequently carbonized by multistep pyrolysis to obtain the NPM catalyst while retaining the small particle size. The catalyst has good performance and promising durability for fuel cell applications. The fuel cell performance under a 0.2 MPa air atmosphere at 80 °C of 1.0 A cm<sup>-2</sup> at 0.46 V is especially remarkable and better than that previously reported.

**Keywords:** N-doped carbon / Oxygen Reduction / Fe/N/C Catalyst / Precipitation Polymerization

### 1. Introduction

Polymer electrolyte fuel cells (PEFCs) have received a great deal of attention due to their high energy conversion efficiency and have been commercialized in automobile and combined heat and power (CHP) applications. In commercialized PEFCs, both the anode and cathode, which oxidize hydrogen and reduce oxygen, respectively, utilize platinum-based catalysts to ensure a sufficiently high reaction rate. However, the cost and scarcity of platinum is a major obstacle to the globalization of PEFCs; therefore, it is necessary to develop non-precious metal (NPM) cathode catalysts. Since Jasinski discovered the catalytic activity of cobalt phthalocyanine<sup>1</sup> for the oxygen reduction reaction (ORR) and Jahnke *et al.* reported the heat treatment of cobalt dibenzotetraazaannulene (CoTAA),<sup>2</sup> 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.<sup>3-6</sup> Promising fuel cell performance has been reported for several NPM catalysts; however, the majority of these reports involved the use of pure oxygen for the cathode gas. Therefore, considering that air would be utilized for the cathode gas in most practical PEFC applications, it is very important to design the cathode layer to minimize the polarization caused by the transport of oxygen molecules.

In this context, our research group is interested in the morphological control of NPM catalysts to maximize the fuel cell performance under air. Here, we report on a NPM cathode catalyst prepared by the pyrolysis of spherical polyimide nanoparticles that contain small amounts 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.<sup>7</sup> In addition, the morphology of polyimide can be controlled through precipitation polymerization, and the fine particle morphology can be retained after carbonization.<sup>8</sup> Here, we report on the synthesis of fine polyimide

nanoparticles with diameters around 60 nm, and the catalytic performance of the carbonized particles as a cathode material under fuel cell conditions using air.<sup>9</sup>

## 2. Experimental

Figure 1 shows the synthesis route for the preparation of the polyimide nanoparticles. Polyimide nanoparticles with diameters of 60 nm were prepared from pyromellitic acid dianhydride (PMDA) and TAPB (TCI, used as-received) in the presence of *N,N*-dimethyldodecylamine (TCI, used as-received) as a dispersant. A solution of 1,3,5-Tris(4-aminophenyl)benzene (TAPB) in acetone (>99.0%, Wako) was added to a solution of PMDA, Fe(acac)<sub>3</sub> and the dispersant (0.3 wt%) in acetone. The molar ratio of PMDA to TAPB was 1.5:1 and the amount of the Fe species was 2 wt% with respect to the resulting polyimide. The mixture was stirred for 30 min at 0 °C. After evaporation of the solvent, the curing reaction proceeded by heating the poly(amic acid) at 240 °C under evacuation to obtain polyimide nanoparticles.

The prepared polyimide nanoparticles were carbonized by multistep pyrolysis, as reported elsewhere.<sup>10</sup> Briefly, 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). The product was washed with conc. HCl after each of the heat treatments at 600 and 800 °C. The carbonized particles are denoted as Fe/PI(100)-1000-III-NH<sub>3</sub>. Polyimide nanoparticles with diameters of 100 nm, Fe/PI(60)-1000-III-NH<sub>3</sub>, were also prepared by a similar manner but from different precursors reported elsewhere.<sup>8</sup>

The catalytic performance of the prepared catalyst was studied by fuel cell testing using a membrane electrode assembly (MEA) prepared with the Fe/PI(100)-1000-III-NH<sub>3</sub> and Fe/PI(60)-1000-III-NH<sub>3</sub> catalysts by the manner reported elsewhere.<sup>8</sup> The MEA performance was tested at 80 °C by flowing fully humidified hydrogen (300 mL min<sup>-1</sup>) into the anode side and fully humidified oxygen or air into the cathode side (300 mL min<sup>-1</sup>). The absolute pressures of the anode and cathode compartments were maintained at 0.2 MPa, unless otherwise stated. *I-V* polarization curves were measured by recording the cell voltages after holding the current density with an electronic load unit (PLZ164WA, Kikusui).

## 3. Results and Discussion

Figure 2 shows the FE-SEM image of the polyimide prepared by the manner shown in Figure 1. This synthesis resulted in polyimide nanoparticles with diameters of approximately 60 nm. The obtained Fe-containing polyimide nanoparticles were carbonized by multistep pyrolysis, where the Fe species catalyzes carbonization up to 600 °C and excess Fe species are removed before treatment at even higher temperatures to minimize the loss of nitrogen species at higher temperature.<sup>9</sup> The diameters of the carbonized samples were similar to those of the polyimide particles (Figure 2 right). The chemical composition of the resulting carbon was determined by the CHN elemental analysis and electron probe micro analysis, C: 91.3 wt%, H: trace, N: 3.0 wt% and Fe: 1.5 wt%, respectively. The BET surface area was determined by the N<sub>2</sub> adsorption as 1217 m<sup>2</sup> g<sup>-1</sup>.

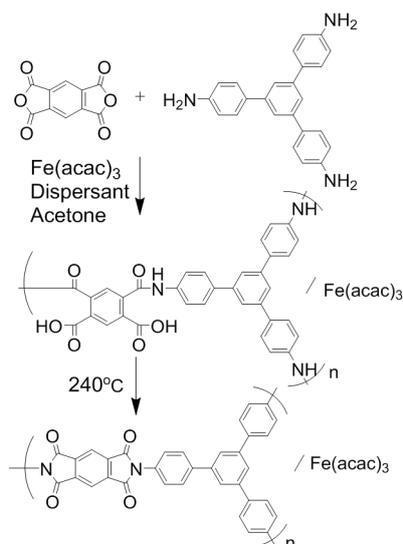


Figure 1. Synthetic route of the polyimide nano-particles.

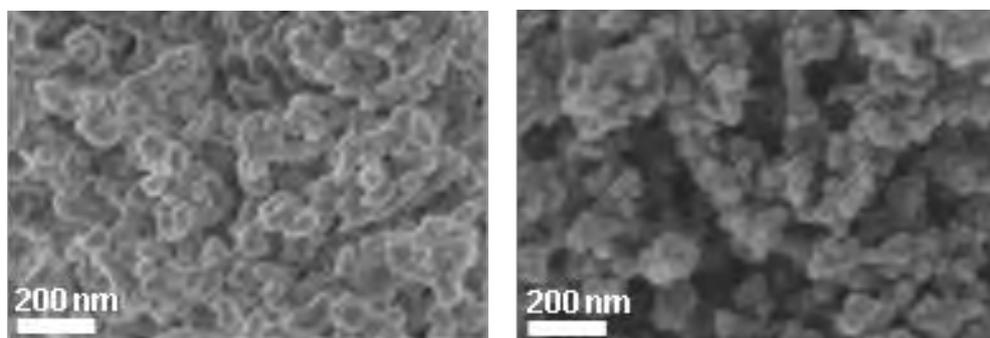


Figure 2. FE-SEM image of the polyimide nano-particles before (left) and after (right) the carbonization.

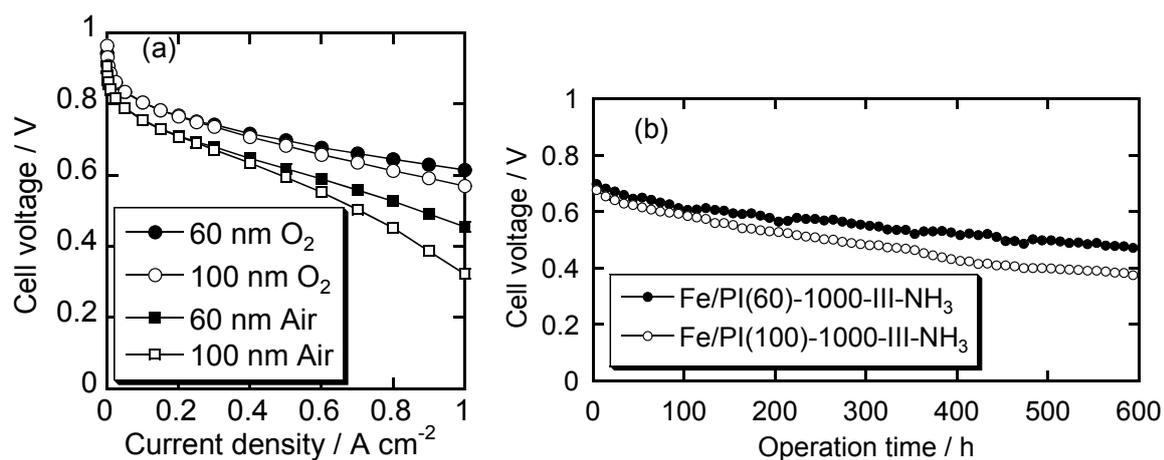


Figure 3. (a) *I-V* performance curves under 0.2 MPa air atmosphere the Fe/PI(100)-1000-III-NH<sub>3</sub> and Fe/PI(60)-1000-III-NH<sub>3</sub> cathode catalysts. Anode: PtRu/C catalyst with 0.4 mg-PtRu cm<sup>-2</sup> loading, humidified H<sub>2</sub> at 80 °C. Cathode: 4 mg cm<sup>-2</sup> catalyst loading, pure or balanced O<sub>2</sub> humidified at 80 °C. Electrolyte: Nafion NR211. *T*: = 80 °C. (b) Cell voltage stability curves at 0.2 A cm<sup>-2</sup> with air as the cathode gas.

The catalysts were tested under practical fuel cell conditions. Figure 3a shows *I-V* performance curves for the membrane electrode assembly (MEA) prepared using Fe/PI(100)-1000-III-NH<sub>3</sub> and Fe/PI(60)-1000-III-NH<sub>3</sub> as cathode catalysts. The MEA with the Fe/PI(100)-1000-III-NH<sub>3</sub> cathode showed open circuit voltages of 0.96 and 0.90 V under pure O<sub>2</sub> and air, respectively, and the current density reached 1 A cm<sup>-2</sup> at 0.57 V (O<sub>2</sub>) and 0.32 V (air). The MEA with the Fe/PI(60)-1000-III-NH<sub>3</sub> cathode showed similar open circuit voltages of 0.94 V (O<sub>2</sub>) and 0.90 V (air), but higher voltages of 0.62 V (O<sub>2</sub>) and 0.46 V (air) at a current density of 1 A cm<sup>-2</sup>. The performance of the MEA with Fe/PI(60)-1000-III-NH<sub>3</sub> under pure O<sub>2</sub> is similar to that of the state-of-the-art NPM cathodes.<sup>4</sup> To the best of our knowledge, the performance of the Fe/PI(60)-1000-III-NH<sub>3</sub> catalyst cathode under an air atmosphere is better than any other reported. Figure 3b shows the changes in the cell voltage during operation at 0.2 A cm<sup>-2</sup> for 600 h. Although the cell voltage gradually decreased, the cells were successfully operated for 600 h. To our knowledge, these are some of the longest durability tests performed using NPM cathode catalysts, whereas most of the state-of-the-art NPM catalysts are significantly degraded within 100 h under practical fuel cell conditions. Thus, the durability demonstrated for the NPM catalyst cathodes in this study is quite promising.

#### 4. Conclusions

A highly active NPM cathode catalyst, Fe/PI(60)-1000-III-NH<sub>3</sub>, was successfully synthesized by the pyrolysis of an Fe-containing polyimide precursor prepared from PMDA and TAPB. This catalyst demonstrated good fuel cell performance and promising durability, especially with air as the cathode gas. The reaction mechanism will be discussed in the presentation, accompanied by detailed spectroscopic data.

**Acknowledgement.** This study was financially supported by NEDO.

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