Oxygen reduction reaction catalysis by Fe/N/C catalyst from polyimide nano-particles

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Abstract: The development of a non-precious (NPM) metal cathode catalyst is extremely important to achieve globalization of polymer electrolyte fuel cells. 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, and subsequently carbonized by multistep pyrolysis to obtain the NPM catalyst. The fuel cell performance with the prepared catalyst under a 0.2 MPa air atmosphere at 80 °C of 1.0 A cm^{-2} at 0.46 V is especially remarkable and better than those previously reported.
Keywords: Fuel cell, Precious-Metal-Free, Electrochemistry.

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. 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.

In this context, our research group is interested in Fe/N/C cathode catalysts prepared from polyimide nano-particles. 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.

2. Experimental

Figure 1a shows the synthetic route for the preparation of the polyimide nanoparticles. Polyimide nanoparticles with diameters of 60 nm were synthesized by precipitation polymerization of pyromellitic acid dianhydride (PMDA) and 1,3,5-tris(4-aminophenyl)benzene (TAPB) in the presence of $Fe(acac)_3$ and *N,N*-dimethyldodecylamine, followed by a curing reaction at 240 °C[1]. The prepared polyimide nanoparticles were carbonized by multistep pyrolysis, as reported elsewhere[2]. 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(60)-1000-III-NH_3. Polyimide nanoparticles with diameters of 100 nm, Fe/PI(100)-1000-III-NH_3, were also prepared by a similar manner but from different precursors reported elsewhere[3].

The catalytic performance of the prepared catalyst was studied by fuel cell testing using a membrane electrode assembly (MEA) prepared with the NPM cathode catalysts by the manner reported elsewhere[1]. The MEA performance was tested at 80 °C by flowing fully humidified hydrogen (300 mL min^{-1}) into the anode side and fully humidified oxygen or air into the cathode side (300 mL min^{-1}). The absolute pressures of the anode and cathode compartments were maintained at 0.2 MPa.

3. Results and discussion

Figure 1b and 1c shows the FE-SEM images of the polyimide nano-particles before and after the carbonization. It is clear that polyimide nano-particles with 60 nm of diameter was successfully obtained and its morphology was retained even after the high temperature treatment.

Figure 2 shows the fuel cell performances of the synthesized NPM cathode catalysts. The difference between the performances of 60 and 100 nm of catalysts was large in the *I-V* curves with air, suggesting the smaller particle size contributes the diffusion of oxygen in the catalyst layer. The cells were successfully operated over 600 h, and the smaller particle size also contributed the durability of the fuel cell. This is may be relevant to the 2+2 oxygen reduction pathway consisting of 2 electron reduction to form H_2O_2, followed by further 2 electron reduction to form H_2O[4].

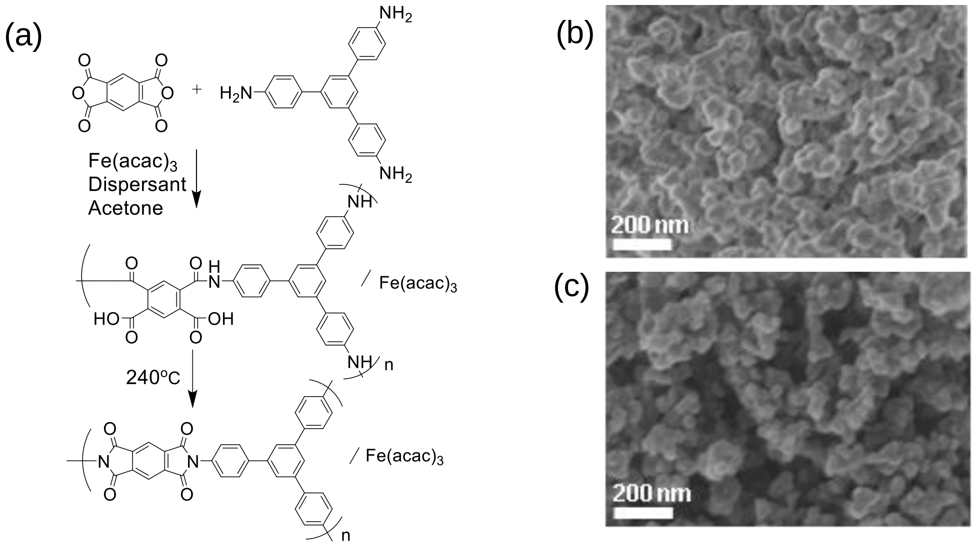

Figure 1. (a) Synthetic route of polyimide-nano particles and the FE-SEM images of them (b) before and (c) after the carbonization.

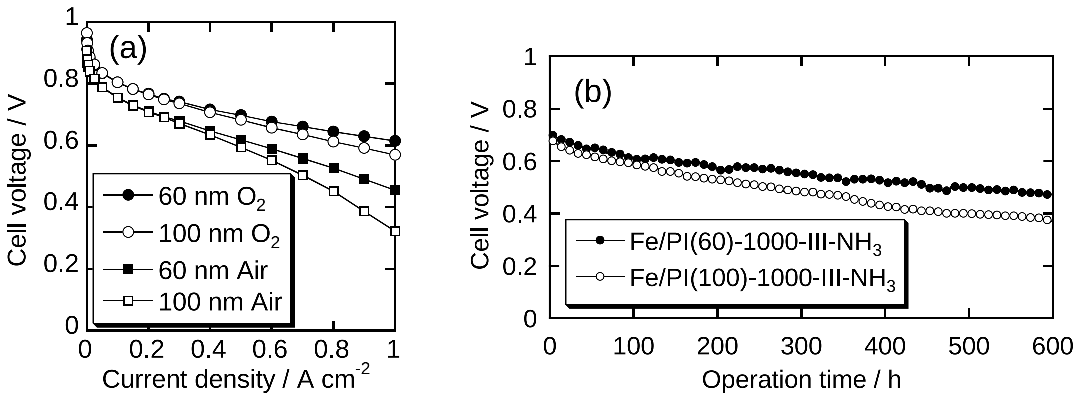

Figure 2. (a) *I-V* performance curves under 0.2 MPa atmosphere the Fe/PI(100)-1000-III-NH_3 and Fe/PI(60)-1000-III-NH_3 cathode catalysts. Anode: PtRu/C catalyst with 0.4 mg-PtRu cm^{-2} loading, humidified H_2 at 80 °C. Cathode: 4 mg cm^{-2} catalyst loading, pure or balanced O_2 humidified at 80 °C. Electrolyte: Nafion NR211. *T*: = 80 °C. (b) Cell voltage stability curves at 0.2 A cm^{-2} with air as the cathode gas.

4. Conclusions

A high performance NPM cathode catalyst for PEFCs has been successfully prepared by the carbonization of polyimide-nano particles. The fuel cell performance with the prepared catalyst under a 0.2 MPa air atmosphere at 80 °C of 1.0 A cm^{-2} at 0.46 V is better than those previously reported. Further studies will be done to improve the catalytic activity and durability, and to clarify the reaction mechanism.

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References

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