Short communication

Preparation of carbon alloy catalysts for polymer electrolyte fuel cells from nitrogen-containing rigid-rod polymers

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ARTICLE INFO

ABSTRACT

'Carbon Alloy Catalysts' (CAC), non-precious metal catalysts for the oxygen reduction reaction (ORR), were prepared from various kinds of nitrogen-containing rigid-rod aromatic polymers, polyimides, polyamides and azoles, by carbonization at 900 °C under nitrogen flow. The catalytic activity for ORR was evaluated by the onset potential, which was taken at a current density of $-2\,\mu A\,cm^{-2}$. Carbonized polymers having high nitrogen content showed higher onset potential. In particular, CACs derived from azole (Az5) had an onset potential of 0.8 V, despite being was prepared without any metals.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted increasing interest in recent years due to their high efficiency of power generation, from clean energy sources. It had seemed that the platinum catalyst used in both electrodes was indispensable for the electrochemical reactions in PEFCs. However, the Pt catalyst prevents commercialization of PEFCs because of its limited availability and high price. Consequently, the development of alternative catalysts is an essential issue for PEFCs. During the past few decades, significant progress has been made in the synthesis, performance, and understanding of the oxygen reduction reaction (ORR), for non-Pt catalysts in PEFC cathodes [1–6].

Boron and nitrogen atoms are useful n and p type dopants for electro active compounds [7,8]. Ozaki et al. demonstrated that ORR catalysts, prepared from boron and nitrogen-doped carbons [9].

Recently, several groups have reported carbon-based catalysts with high ORR activity. Dodelet et al. prepared catalysts by wet impregnation of carbon black with iron(II) acetate, followed by heat treatment in NH_3 [10]. They suggested that active sites contained iron cations coordinated by pyridinic nitrogen functionalities in the interstices of graphitic sheets.

Popov et al. reported nitrogen-modified carbon composite catalysts, prepared via pyrolysis of Co–Fe–N chelate complex, as supported on carbon black [11,12]. Ozaki et al. prepared catalysts from resin mixed with Fe or Co phthalocyanine by carbonization at several temperatures [13,14]. These catalysts can be termed Carbon Alloy Catalysts (CAC) because they are composed of a mixture of carbon, nitrogen and metals. Both Popov's and Ozaki's groups applied acid-washing treatment to remove metal on the surface of catalysts. After the removal of metal, the catalysts still showed high ORR activity. These papers implied that presence of metals in the preparation of the catalysts was essential to obtain high activity. However, there are few detailed discussions about the activity of catalysts prepared from metal-free, nitrogen-containing polymers [15].

Recently, the active site of CACs was proposed to be carbon atoms neighboring graphite-like nitrogen atoms along the zig-zag edge of graphite, in a computational study [16] by Ikeda et al, and in X-ray absorption analysis by Niwa et al. [17]. Additionally, Popov et al. suggest that pyridinic and graphite-like nitrogen act as the active site for ORR [12].

We considered that carbonization of nitrogen-containing aromatic polymers with well-defined chemical structures, could clarify the correlation between the starting material and the carbonized samples. We expected that highly active catalysts could be obtained from optimized polymer structures, without using metals. Rigid-rod polymers are attractive materials for use in high-performance structural applications, due to their outstanding physical and mechanical properties. Their structures consist mainly of aromatic carbons and nitrogen atoms. Recently, the carbonization of aromatic polymer fibers was investigated to obtain activated, nitrogen-containing carbon fibers [18–21].

In this paper, CACs were prepared from nitrogen-containing aromatic rigid-rod polymers via a metal-free carbonization process. We found that CACs prepared from azoles have high ORR activity.

2. Experimental

2.1. Preparation of polymers

Polyimides (PI), polyamides (PA) and azoles (Az) were prepared by the usual polycondensation methods [22–26], as shown in Fig. 1. Nine kinds of PIs, two kinds of PAs, and five kinds of Azs were prepared, as summarized in Fig. 2. Inherent viscosities were measured with an Ubbelohde type viscometer at 30 °C as a rough indication of the molecular weight of the polymers.

2.1.1. Preparation of polyimide: poly (para-phenylene pyromellitic imide) (PI1)

To a solution of 5.54 g para-phenylenediamine in 800 ml of *N,N*-dimethylacetamide (DMAc), 7.74 g of pyromellitic dianhydride was added, and then the reaction mixture was stirred at 0 °C for 1 h, then at 25 °C for 1 h. After the reaction, the thus-obtained polymer solution was poured into a large amount of deionized water and methanol. The precipitated polyamic acid (the precursor of polyimide) was isolated by filtration and dried at 120 °C for

12 h in a vacuum oven. Inherent viscosity (η_{inh}) of the polyamic acid (measured in 0.5 g dl^{-1} of DMAc solution) was 0.1 dl g^{-1}. Finally, to obtain polyimide, the polyamic acid was heated at up to 350 °C for times of up to 1 h. The obtained polyamic acid was annealed at 350 °C for 1 h to obtain polyimide, via the ring-closure reaction.
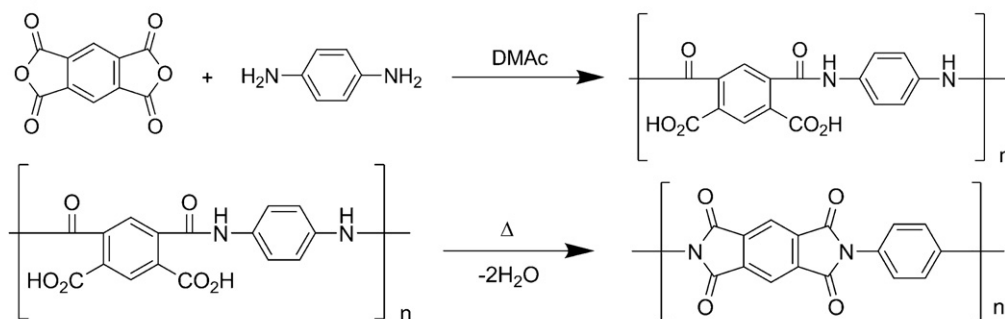
2.1.2. Preparation of polyamide: poly (meta-phenylene isophthalamide) (PA2)

To a solution of 22.0 g meta-phenylenediamine in 250 ml of *N*-methyl-2-pyrrolidone (NMP), 41.3 g of isophthaloyl chloride was added. After the reaction mixture had been stirred at 0 °C for 1 h, then at 50 °C for 2 h, 15.1 g of calcium hydroxide was added to complete the reaction. The thus-obtained polymer solution was poured into a large amount of deionized water. The precipitated polymer was isolated by filtration and dried at 120 °C for 12 h in a vacuum oven. The inherent viscosity (η_{inh}) of the polyamide (measured in 0.5 g dl^{-1} of sulfuric acid solution) was 1.36 dl g^{-1}.

2.1.3. Preparation of azole: poly{2,6-diimidazo[4,5-b:4′,5′-e]pyridinylene-1,4-(2,5-dihydroxy) phenylene} (Az5)

In a flask, 62.54 g of polyphosphoric acid and 14.76 g of phosphorus pentoxide were added to 22.88 g of the 2,3,5,6-tetraaminopyridine/2,5-dihydroxyterephthalaic acid salt, and they were stirred and mixed at 100 °C for 1 h. The temperature of mixture increased to 140 °C over 2 h, when it was stirred for 1 h. Then, the reaction temperature of mixture increased to 180 °C over 1 h, and at 180 °C it was allowed to react for 5 h, forming a dope. The thus-obtained dope contained 18 g of polymer and 82 g of polyphosphoric acid, and when measured through a polarizing microscope, it exhibited liquid crystallinity. The dope was re-precipitated in water and washed with water, leaving the polymer. The inherent viscosity (η_{inh}) of the azole (measured in 0.03 g dl^{-1} of methanesulfonic acid solution) was 5.5 dl g^{-1}.
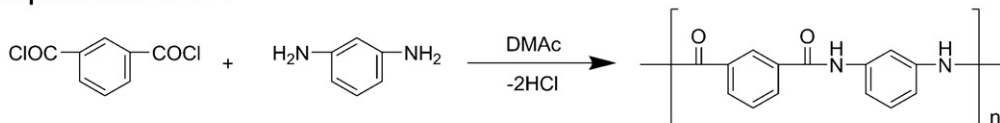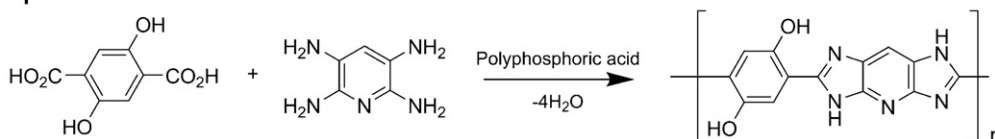

Fig. 1. Typical example of the preparation of polyimide (PI), polyamide (PA) and azole (Az) polymers.
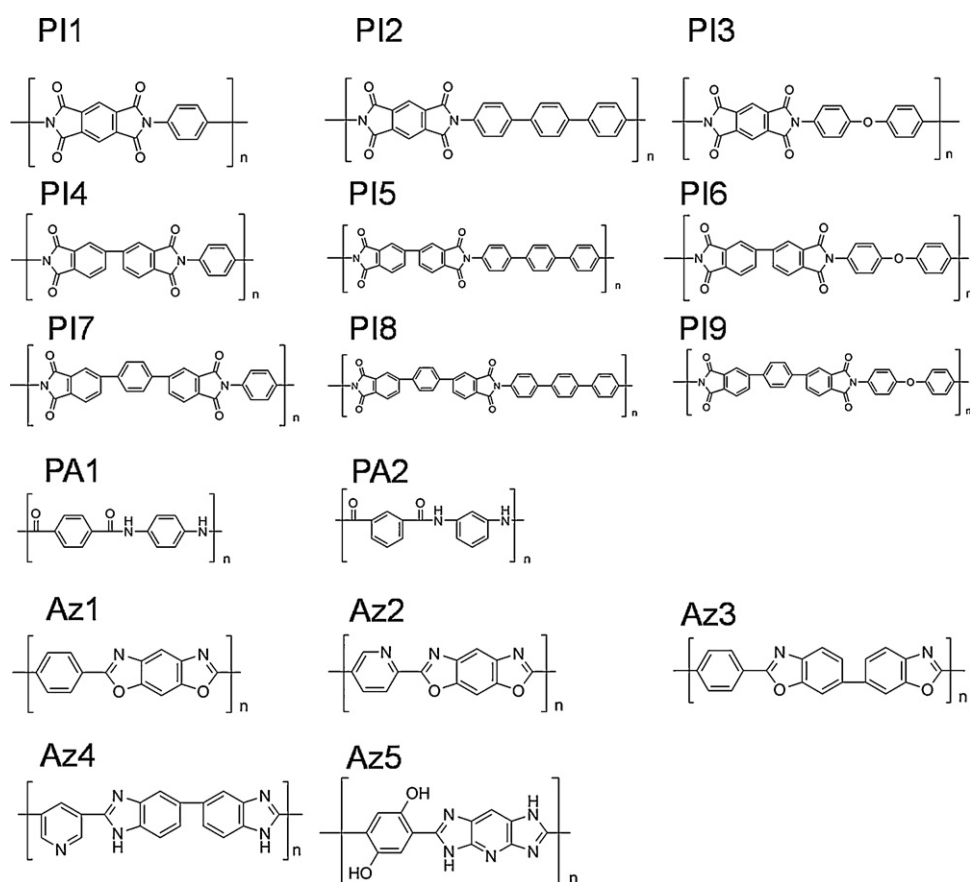
Fig. 2. Prepared PI, PA and Az samples.

2.2. Preparation of carbon alloy catalysts

The obtained polymers were carbonized at 900 °C for 1 h under nitrogen flow. After carbonization, the samples were pulverized using ball mill equipment.

2.3. Electrochemical measurement and structural characterization

The ORR activity was evaluated by rotating disk electrode voltammetry using the prepared carbons as the working electrodes, with a rotation rate of 1500 rpm, at 25 °C. Fabrication of electrodes and measurements of linear sweep voltammetry for oxygen reduction voltammograms followed the same procedure as Ozaki et al. [9]. The onset potential (the potential at which a current density of $-2 \, \mu A \, cm^{-2}$ is recorded) was taken from the oxygen reduction voltammograms. Elemental analysis was performed on a PerkinElmer 2400 Series II CHN/O Analyzer. N1s core-level X-ray photoelectron spectroscopy (XPS) was measured with a PerkinElmer X-ray Photoelectron Spectrometer 5500MT. The specific surface area of the catalysts was determined by N_2 adsorption using a volumetric adsorption measurement instrument (Bel Japan, Belsorp-mini II).

3. Results and discussion

3.1. Nitrogen content of carbonized nitrogen-containing rigid-rod polymers

Fig. 3 shows the nitrogen content of PI samples before and after carbonization. The nitrogen content of the carbonized sam-

ple increases linearly with increasing nitrogen content of the PIs. Approximately 60% of nitrogen atoms were retained after carbonization at 900 °C.

3.2. Onset potential of ORR of carbonized samples

The ORR activity of the carbonized samples was evaluated using the onset potential. Voltammograms and catalytic activity of the carbonized PI, PA and Az samples are shown in Fig. 4 and Table 1. The onset potentials and current density of carbonized samples with different nitrogen contents are summarized in Figs. 5 and 6. These results show that carbonized azoles which had high amounts of nitrogen showed higher onset potentials and current densities. The BET surface area of the carbonized PI, PA and Az samples, evaluated by N_2 adsorption, is summarized in Fig. 7. Although carbonized
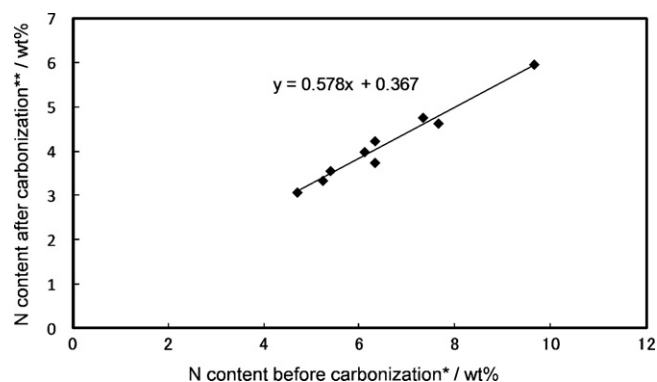

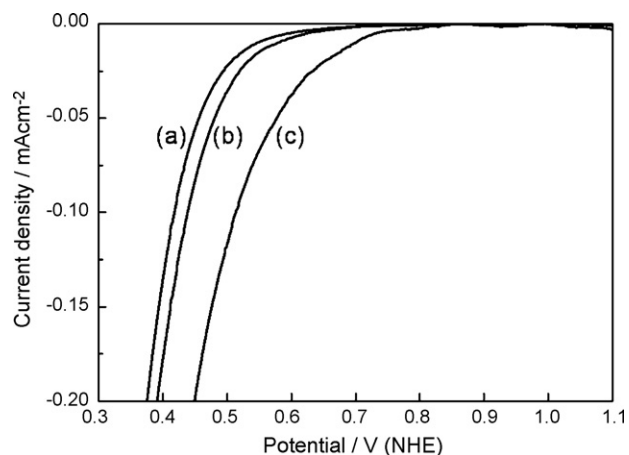**Fig. 3.** Nitrogen content of PIs before and after carbonization.

Fig. 4. Voltammogram of carbonized samples (a) PI3 (b) PA1 (c) Az5.

Table 1
Contents of nitrogen and catalytic activities of carbonized samples.

	N/C atomic ratio	Onset potential[a] (V)	Current density[b] (μA cm^{-2})
PI3	0.05	0.65	−24
PA1	0.07	0.73	−41
Az5	0.08	0.80	−120

[a] Potential measured at −2 μA cm^{-2}.
[b] Current density measured at 0.5 V.

azole has a relatively small surface area compared with PI samples, most of carbonized azoles display higher catalytic activity than carbonized PI samples. Additionally, even though these polymers were carbonized without any metal compounds, Az5 (for structure see
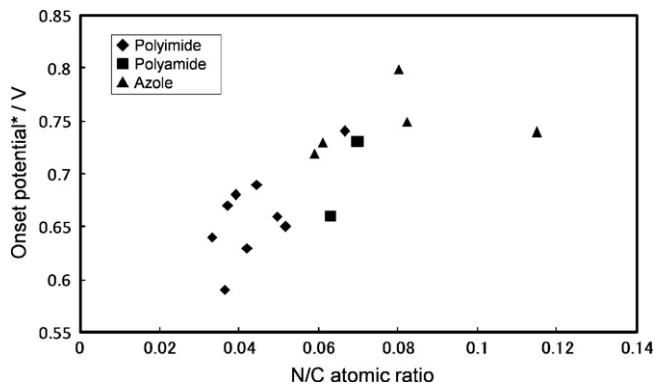

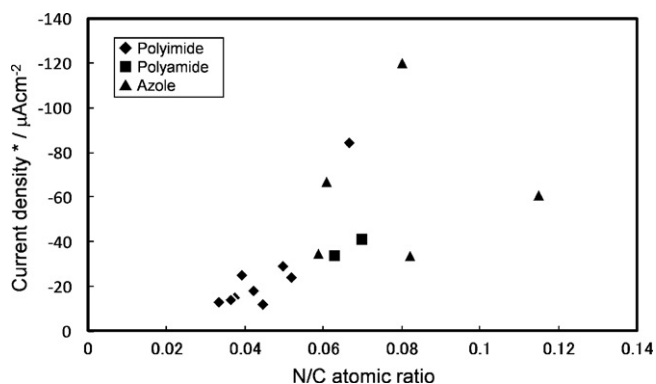**Fig. 5.** Onset potential of carbonized samples with different nitrogen contents.

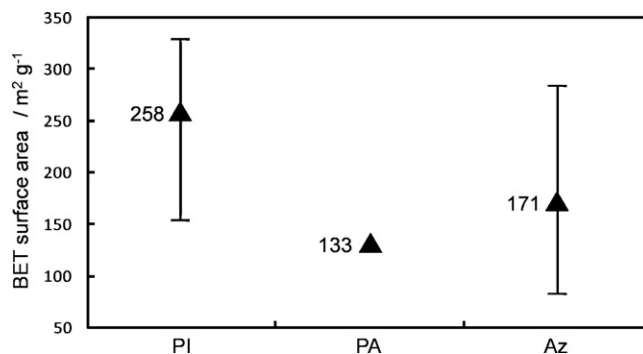**Fig. 6.** Current density of carbonized samples with different nitrogen contents.

Fig. 7. Specific surface area of the carbonized PI, PA and Az samples.

Fig. 2) showed very high catalytic activity, with an onset potential of over 0.8 V.

We compared this to Ozaki et al.'s results [13], in which phenolic resin and Fe/Co phthalocyanine were carbonized to form nano-structured nitrogen-doped carbon. These macrocycle-derived CACs displayed onset potential of 0.8 V (at −10 μA cm^{-2}) which are higher than that of carbonized Az5, prepared without Fe or Co (0.73 V measured at 10 μA cm^{-2}). However, our results displayed higher onset potentials than carbonized furan resin prepared from metal-free phthalocyanine (0.52 V at −10 μA cm^{-2}). The Formation of nanostructures by heat treatment of nitrogen-containing polymers and metal incorporation with these polymers will be discussed in separate paper.

3.3. XPS study of carbonized samples

Since CACs is heterogeneous catalyst, it is important to analyze surface structure of CAC. XPS can allow quantitative analysis of the nitrogen contents on the surface area.

Fig. 8 shows the XPS N1s peak for the carbonized polymers. Proportions of nitrogen-oxide (N-1), graphite-like nitrogen (N-2) pyrrolic nitrogen (N-3) and pyridinic nitrogen (N-4) can be observed by peak fitting [27,28]. Contents of these nitrogen and catalytic activity of carbonized sample are summarized in Table 2. As is the case with elemental analysis, carbonized azoles which showed a high onset potential contained a large amount of nitrogen. Consequently, due to an increase of nitrogen content, carbonized azoles posses also a large amount of graphite-like nitrogen of which neighboring carbon is considered as active site [16,17].

From these results, it should be concluded that carbonized azole is the best candidate for CACs among the nitrogen-containing rigid-rod polymers. Its high activity may be due to the fact that the Az5 structure already contains the N–C–N configuration in the polymer structure also observed in the zig-zag edge of graphite.
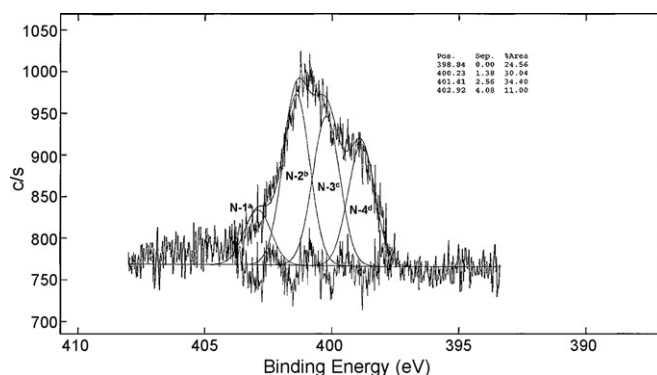

Fig. 8. N1s X-ray photoelectron spectra for PI2.

Table 2
Onset potential and proportion of nitrogen of CAC measured by XPS.

	Onset potential[a] (V)	XPS analysis[b] ($\times 10^{-2}$)				
		N/C	N-1/C	N-2/C	N-3/C	N-4/C
PI-2	0.64	4.70	0.51	1.61	1.41	1.15
PI-8	0.66	0.97	0.59	0.38	0.28	0.16
PI-9	0.58	2.83	2.07	0.75	1.05	0.60
PA1	0.74	4.83	0.32	1.44	1.59	1.44
Az1	0.79	6.66	0.72	2.12	2.11	1.70
Az5	0.81	5.31	0.73	2.01	1.04	1.04

[a] Potential measured at $-2\,\mu A\,cm^{-2}$.
[b] N-1: nitrogen-oxide, N-2: graphite-like nitrogen, N-3: pyrrolic nitrogen, N-4: pyridinic nitrogen.

4. Conclusion

In this paper, carbon alloy catalysts were prepared starting from various nitrogen-containing rigid-rod aromatic polymers, polyimides, polyamides and azoles. Despite the fact that these catalysts were prepared without metals, the onset potential for ORR was surprisingly high. In particular, the carbonized azole, poly {2,6-diimidazo [4,5-b:4′,5′-e] pyridinylene-1,4-(2,5-dihydroxy) phenylene}, showed an onset potential of 0.8 V. The high ORR activity may derive from the chemical structure of benzimidazole, in which the N–C–N configuration is already established as that in the zig-zag edge of graphite.

Acknowledgements

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