Preparation of BN-doped carbon blacks by mechanochemical alloying of carbon and h-BN and its use as a catalyst for the oxygen reduction

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BN-doped carbon blacks were prepared by mechanochemical alloying of a carbon black and h-BN (h-BN doping ratio : 0 ~ 50 at %). The structure, the surface chemical states and the catalytic activity for an electrochemical oxygen reduction reaction of the prepared carbons were investigated. XRD and TEM studies revealed the following influences of h-BN on the structure of the carbon black ; i.e. the reduction in the d_{002} -spacing and the loss of the alignment of the graphene layer in the primary particles of the carbon black. Detailed studies were conducted for the 20 at % BN-doped carbon black, since incomplete alloying was observed obviously for the samples with higher doping levels than 33 at %. XPS studies proved the formation of B-C and N-C bonds as well as B-N-C moieties, which indicated a mechanochemical reaction between the carbon black and h-BN, took place during mechanical treatment. Hence, the mechanical treatment of carbon black and h-BN could provide BN-doped carbon blacks. Increases in the activities of carbons for the oxygen reduction reaction were observed by the mechanical treatment ; i.e. only a simple treatment without h-BN could increase the activity by 17 times that of the pristine carbon black, and a further 10 fold enhancement was observed for the BN-doped carbon.

KEYWORDS : Carbon alloy, Mechanochemical alloying, Boron nitride, X-ray photoelectron spectroscopy, Electrochemical reduction of oxygen

1. Introduction

Exploration of a non-platinum catalyst for an oxygen reduction reaction (ORR) in polymer electrolyte membrane fuel cells (PEMFC) is not only an urgent issue for the practical utilization of fuel cells, but is also a compelling issue in the field of material science. Several candidates have been proposed including pyrolyzed N₄-M complexes¹⁾⁻⁴⁾, ceramics such as carbides^{5), 6)} and palladium⁷⁾. We have been interested in the design of functional carbon materials, by controlling the carbonization processes⁸⁾. We have recently reported that introducing "edge-nitrogen" to the carbon surface is an effective way to give ORR activity to carbons⁹⁾. Furthermore, it was also revealed that the activity was enhanced by the simultaneous doping of boron and nitrogen to carbon materials (BN-doped carbons)¹⁰⁾.

Mechanochemical alloying is expected to be a new innovation in the production of non-conventional materials, which has also

been applied to graphite¹¹⁾⁻¹⁶⁾ and carbon nanotubes^{17), 18)}, in order to construct novel nano carbon structures^{13), 14)} or to improve the performance of carbons in such applications as lithium battery capacity^{15), 16)}. Russian co-authors, Bokhonov and his group, have reported the formation of nanostructures in carbon materials by applying this technique to carbon and metal particles¹⁹⁾. They also studied the mechanical reaction between Fe and h-BN²⁰⁾. Application of this technique in the production of BN-doped carbon materials is of great interest regarding the potential development of new type carbon alloys that have ORR activities. For example, Yao *et al.* reported the formation of amorphous B-C-N semiconductor by mechanical milling of h-BN and graphite, where the mixing ratio was 1 : 1²¹⁾. Their study surely shows this technique being promising for the preparation of new functional carbon materials.

In the present paper, we will describe the preliminary results in the formation of BN-doped carbons which were formed using a planetary ball mill capable of generating 60 g of gravity acceleration.

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Specifically, we are going to report the formation of B-C and N-C bonds as well as B-N-C moiety by simple mechanical treatment of a carbon black and h-BN. We also report signs of enhancement in ORR activity of the BN-doped carbon.

2. Experimental

A carbon black (Biisk soot plant, Russia, TY 3841558-97) and h-BN (UNICHIM Ekaterenburg, Russia TY 2112-003-49534204-2002) were loaded into a stainless steel vial (250 ml) together, where the air was exchanged by Ar gas. The mixture was then subjected to mechanochemical doping using a 60 g planetary ball mill. The details of the mill are described elsewhere²²⁾. The starting materials to be milled were the mixtures of the carbon black and the h-BN with different mixing ratios of 20, 33 and 50 at % of h-BN. These were continually milled for 10 min at a constant gravity of 60 g. The sample to ball ratio was kept at 1 : 20 for all preparations. After the treatment, the sample was acid washed with HCl in order to remove the metal contaminant introduced during the treatment. The obtained sample is hereafter referred to as MA-x, where x stands for the mixing ratios of h-BN. A reference sample was prepared by ball milling the genuine carbon black under the same treatment conditions (MA-0).

Characterization of the carbons was performed by X-ray powder diffraction (XRD, RINT2100/PC, Rigaku Corp.), X-ray photoelectron spectroscopy (XPS, ESCA-5600, Perkin-Elmer) and transmission electron microscopy (TEM, JEM2010, JEOL). The ORR activity of the carbons was studied using the rotating disk electrode voltammetry technique (details shown elsewhere^{8), 9)}. The conditions are briefly presented below. The working electrode was prepared by pasting the carbon samples on a glass-like carbon electrode (3 mm ϕ) with Nafion® binder. The reference and counter electrodes were Ag/AgCl and a platinum wire, respectively. The electrolyte was 1 mol dm⁻³ H₂SO₄ aqueous solution saturated with O₂ at room temperature. Hydrodynamic voltammograms were recorded by rotating the electrode at 1500 rpm and by sweeping the potential from the open circuit potential to -0.1 V vs. Ag/AgCl at 0.5 mV s⁻¹. Hereafter the potentials are expressed with respect to NHE reference.

3. Results and discussion

Fig.1 shows the X-ray diffraction patterns of the mechanically treated samples. The reference, MA-0 showed a broad (002) diffraction peak of carbon at $2\theta = 24.5^\circ$ (d_{002} -spacing of 0.363 nm), which was smaller than the diffraction angle of the pristine carbon black ($2\theta = 25.0^\circ$). The BN-doped samples showed (002) diffractions at higher diffraction angles, i.e. MA-20 showed it at $2\theta = 25.5^\circ$ (d_{002} -spacing of 0.349 nm) and the angle seemed to be shifted to higher angles with the doping level. Such contraction in the *c*-axis of the

Fig.1 X-ray diffraction patterns in (002) region of the prepared sample.

carbon structure was reported by Zhang *et al.*²³⁾, where carbon was also mechanically treated with h-BN. It should also be noted that the presence of the residual h-BN crystallites in the BN-doped carbon blacks evidenced by sharp diffractions at $2\theta = 26.5^\circ$, of which the intensity increased with the doping level. This peak is considered to be a small crystal of h-BN, since this diffraction angle was close to the diffraction angle of 26.62° obtained from the genuine h-BN crystal.

Typical transmission electron micrographs of the mechanically treated samples are shown in **Fig.2**. In the case of MA-0, the mechanical treatment did not produce significant changes in the carbon structure, as shown **Fig.2** (a), since a typical structure of carbon blacks was maintained; i.e. concentric alignment of discrete graphene layers along the surfaces of the primary particles. Conversely, this concentric feature was lost in the BN-doped carbon blacks as shown in **Fig.2** (b) - (d); i.e. they showed randomly oriented graphene layers in the primary particle. Another interesting observation was the formation of slightly aligned layers in the BN-doped carbon blacks as indicated by the arrows, of which the population increased with the doping level.

The formation of nanostructures seemed to occur with some regularity in the initial stage of ball milling of graphites. The formation of a scrolled structure reported by Li *et al.* is an example of this phenomenon¹⁶⁾. Zhang *et al.* reported the contraction of the d_{002} -spacing of carbon by mechanical treatment with h-BN, and they inferred the occurrence of a formation of this mixed layer which was composed of graphene and h-BN sheets²³⁾. The slightly aligned layers in the BN-doped carbon blacks can be concluded as being resultant of such an effect. There are two possible ways in which this structure is formed; one is small crystallites of h-BN and another is the mixed layers of graphene and h-BN, as inferred by Zhang. These layers do not correspond to the sharp X-ray diffractions

Fig.2 TEM micrographs of the prepared samples. (a) MA-0, (b) MA-20, (c) MA-33 and (d) MA-50.

Table 1 Preparation conditions and the surface chemical composition by XPS for the prepared samples.

sample	BN (at%)	gravity (g)	time (min)	XPS composition		
				B/C	N/C	O/C
MA-0	0	60	10	0	0	0.12
MA-20	20	60	10	0.07	0.09	0.33
MA-33	33	60	10	0.23	0.17	0.47
MA-50	50	60	10	0.30	0.30	0.35

at $2\theta = 26.5^\circ$ observed for the BN-doped carbons, because the estimated crystallite size from the peak width was too large, approximately 36 nm, to be the slightly aligned layers observed by TEM. Still, the information available is not enough to identify the slightly layered structure observed in the present study, hence further study is required.

The surface chemical compositions by XPS are presented in **Table 1**. Both B/C and N/C ratios increased almost linearly with the doping level and showed similar values. Also non-negligible amount of oxygen was introduced by the ball-milling in the presence of h-BN. Since the milling process was carried out in inert atmosphere, the introduction of oxygen is considered as a result of oxygen capturing from the air when the activated surfaces were exposed to the air.

As shown by the results of XRD and TEM, the samples with higher BN-doping level such as MA-33 and MA-50 were inhomogeneous, probably due to the incomplete alloying of the h-BN and the carbon black. Hence, we decided to conduct further investigation for MA-20 and MA-0 samples. The rest of this paper will be spent for the description of the detailed XPS analyses and electrochemical activity studies.

Fig.3 XPS spectra of the MA-20 sample. (a) B1s and (b) N1s regions.

B1s and N1s XPS spectra of the MA-20 are presented in **Fig.3** (a) and (b), respectively. Although the B1s spectrum appeared to be bimodal, it was divided into four elemental sub-spectra as shown in **Table 2** (a), for the best fitting. The B-I component with the lowest BE was herein assigned as being boron atoms connected to carbon atoms (BN_2C or BC_3 , 189.5 and 189.4 eV, respectively)²⁴. The B-II component was assigned as the boron atoms connected to

Table 2 (a) Assignments of B1s spectrum of MA-20,
(b) Assignments of N1s spectrum of MA-20.

(a)			
	BE (eV)	B/C	Assignment
B-I	189.6	0.027	BN ₂ C, BC ₃
B-II	190.6	0.008	BC ₂ O, h-BN
B-III	191.9	0.03	BCO ₂ , B-N-C
B-IV	193.2	0.005	B-O

(b)			
	BE (eV)	N/C	Assignment
N-I	398.4	0.022	h-BN, Pyridine
N-II	399.2	0.021	B-N-C
N-III	400.3	0.018	Pyrrol/pyridone
N-IV	401.4	0.015	Quaternary
N-V	402.3	0.014	Oxides

two carbon atoms and one oxygen atom, BC₂O²⁵⁾, and h-BN²⁶⁾. The B-III component with the largest B/C content was considered as the boron atoms in BCO₂²⁵⁾ and B-N-C²⁷⁾ moieties. It is probable that the B-IV component could be assigned as B-O bonds²⁴⁾. Thus, the formations of B-C, B-N-C and B-O bonds were confirmed, when the mechanical treatment was performed on a carbon black in the presence of h-BN.

Five sub-spectra were needed for the complete retrieval of the original N1s spectrum, of which the assignments are presented in **Table 2** (b). The N/C fractions assigned to each sub-spectrum were almost the same. The N-I component with the lowest BE can be assigned as pyridinic nitrogen in carbon²⁸⁾ or as h-BN. Since the XRD results showed a visible diffraction peak of h-BN, it is very difficult to determine the major species responsible for N-I. The N-II component was assigned as the B-N-C moieties found in BNC compounds²⁴⁾ or B_xC_yN_z²⁹⁾. The assignments of N-III, N-IV and N-V were pyrrol/pyridone, quaternary and oxide species, respectively²⁸⁾.

An important conclusion observed in the XPS study is the occurrence of a mechanochemical reaction between carbon and h-BN to form B-C and N-C bonds and B-N-C moieties.

The ORR voltammograms of the prepared samples are presented in **Fig.4**. The pristine carbon black showed only a small reduction in current even at the lowest potentials. The mechanical treatment was found to enhance the ORR activity, irrespective of the presence of h-BN, which are evident from the comparison of the voltammograms of MA-0 and MA-20 with that of the pristine carbon black. The effect of the treatment was more evident when the carbon black was mechanically treated with the h-BN dopant. For example, the current densities at 0.3 V vs. NHE were 0.001 mA cm⁻² for pristine, 0.017 mA cm⁻² for MA-0 and 0.19 mA cm⁻² for MA-20. A seventeen fold increase in the ORR current was obtained for MA-0 compared with the pristine sample, hence the mechanical treatment was an effective way to provide ORR activity to carbons. An almost ten

Fig.4 Hydrodynamic voltammograms of the carbons for ORR. For comparison, the result on the previously prepared BN-doped carbons [10] and the result of a commercial 10 % Pt/C catalyst (EC-10, Electrochem. Inc.) are also included.

fold increase was observed when the carbon black was mechanically treated with h-BN.

It is interesting to compare the activity of MA-20 with the BN-doped carbon previously reported in Ref (10), which were prepared by carbonization of poly (furfuryl alcohol) containing B and N source compounds, i.e. BF₃-MeOH and melamine, respectively. The XPS N/C surface ratio of MA-20 was 0.09 as presented in **Table 1**, which was 1.8 times that of the previous BN-doped carbon. However, the ORR activity of the present BN-doped carbon was lower than that of the previous BN-doped carbon. The N1s spectrum of the previous BN-doped carbon was different from the present MA-20; i.e. N-II and N-IV were the two major components in the previous BN-doped carbon. In contrast, all five components were evenly distributed in MA-20. The reduction current observed for the previous BN-doped carbon was 1 mA cm⁻² at 0.3 V vs. NHE, which was approximately five times greater than MA-20. This is a contradiction to the presences of the edge-nitrogen and B-N-C moieties in larger amounts. The explanations for the lower activity of MA-20 than the previous BN-doped carbon are not clear at the present stage. The most striking difference between them was the surface O/C ratios; i.e. the ratio was 0.33 for MA-20 and 0.10 for the previous carbon. One possible explanation is that the surface oxides inhibited the occurrences of the ORR on the surface or the electron conduction between the carbon particles. Also the specific surface area may be an influential parameter on the ORR activity. Further studies are undertaken in our laboratory.

Of course the activity of the present samples are too low to be used in the real PEMFC in the present form, which is clearly observed when the voltammograms are compared with that of a commercial platinum catalyst (EC-10, Electrochem. Inc.) designated as 10 % Pt/C in **Fig.4**; however, we would like to emphasize the fact that the ORR activity can be enhanced by the mechanochemical doping of boron and nitrogen into a carbon material. We believe

there is still some room for improving the activity in, for example, changing the amount of h-BN added to carbon blacks and/or heat-treatment of the carbons. Further investigation into the factors influencing the doping level as well as the heat treatment are now being studied in our laboratory, and the results will soon be reported.

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