# Carbon-based Cathode Materials Doped with a New Borazine Compound for Electrochemical Oxygen Reduction

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A new compound, *B,B′,B″*-tris(4-hydroxyphenyl)-*N,N′,N″*-triphenylborazine (BZ) was prepared as a precursor for carbon-based oxygen reduction catalysts. The mixtures of BZ and phenolic resin were pyrolyzed under N_2 at 1000 °C for 5 h and resulted in a carbonaceous material with high oxygen and boron contents. The oxygen reduction catalytic activity was much improved by the addition of this precursor. The improved catalytic activity is probably due to the oxygen-containing functionalities that are enriched in the presence of boron species.
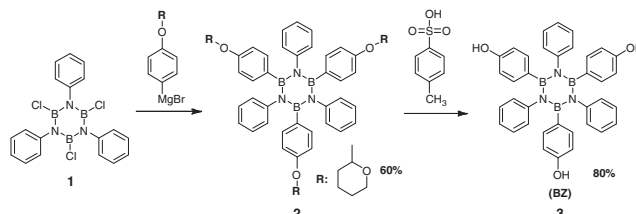
Scheme 1. Synthetic route of *B,B′,B″*-tris(4-hydroxyphenyl)-*N,N′,N″*-triphenylborazine (BZ).

Carbonaceous materials containing hetero atoms such as B and N are called hetero-atom-substituted carbon alloy[1] and have attracted attention since they are expected to have novel properties that are different from those of pure graphite, graphene, or diamond. The B/C/N materials have been widely prepared by chemical vapor deposition (CVD) or solid–gas reaction.[2] Physical and chemical properties of these materials have been investigated, and several applications of the materials to energy devices such as secondary Li ion batteries,[3] semi-conducting materials,[4] and fuel cells[5] have been demonstrated.

Experimental and theoretical studies on doped graphene have suggested the possibility to form both p- and n-type semiconducting graphenes by substituting C atoms with B and N atoms,[6–8] respectively. The dopant atoms can modify the electronic band structure of graphene and affect the conducting properties. More interestingly, B, C, and N can be atomically mixed together to form various semiconducting hexagonal layered structures with varying stoichiometry, such as BCN nanotubes.[9,10] BCN graphitic films (thickness from 100 nm to a few micrometres) have been prepared by thermally decomposing B-, C-, and N-containing precursors by chemical vapor deposition (CVD).[11]

Regarding electrocatalysis, boron-doped carbon materials for oxygen reduction reaction (ORR) was first reported by Ozaki et al.[12] They used a BF_3–MeOH complex as a boron source; however, this suffered from low boron content in the resulting carbon. Our present aim is to explore more effective ways for boron doping. In this context, we have synthesized *B,B′,B″*-tris(4-hydroxyphenyl)-*N,N′,N″*-triphenylborazine (BZ) (compound (**3**) in Scheme 1) as B, N, and O dopant for carbon materials. This paper discusses the properties of the carbon materials prepared from this new borazine dopant.

The BN precursor BZ (**3**) was synthesized by a synthetic route outlined in Scheme 1.[19] *B,B′,B″*-Trichloro-*N,N′,N″*-tri-phenylborazine (**1**) (mp: 270–272 °C) was prepared from boron trichloride and aniline according to a well-known method.[13] This compound was converted into compound **2** by using a Grignard reaction with 4-(tetrahydropyran-2-yloxy)phenylmagnesium bromide. The protective group in compound **2** was removed
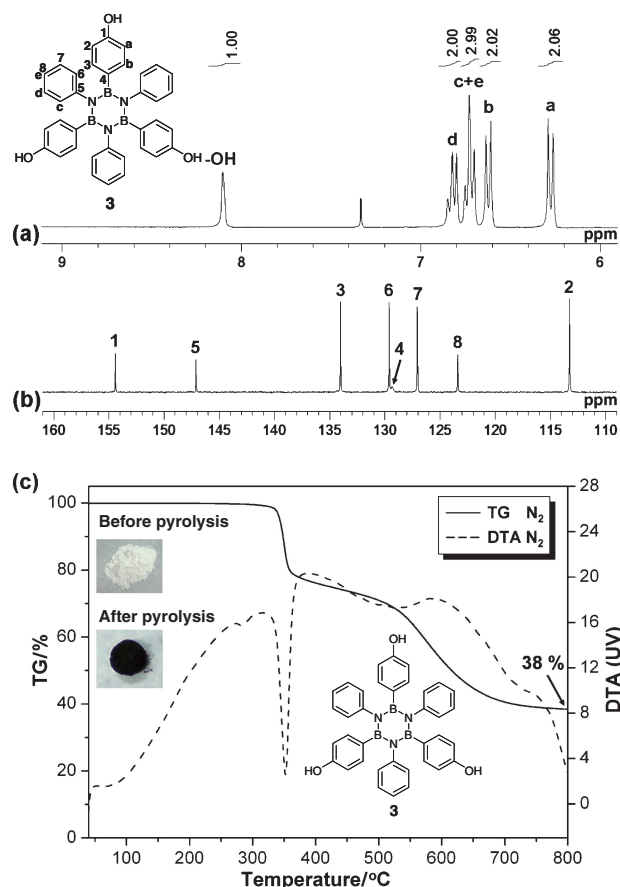
Figure 1. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of BZ (**3**) in $CDCl_3$-*d* with 0.05 mL of MeOH, and (c) TGA curve of BZ (**3**) under a N_2 flow with a heating rate of 20 °C min^{-1}.

with *p*-toluenesulfonic acid, and then BZ (**3**) was obtained. Figure 1 illustrates the ^{1}H NMR and ^{13}C NMR spectra and thermal properties of compound **3**. Assignments of each carbon and proton are also given in these figures and agree well with the
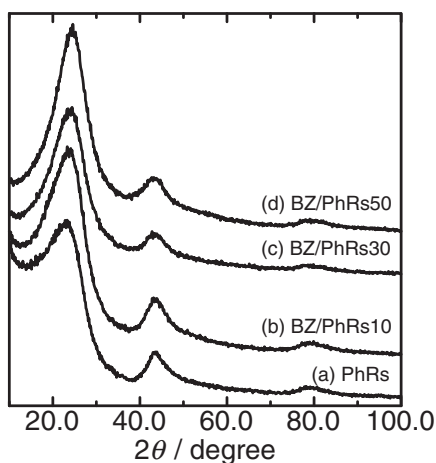
Figure 2. XRD patterns of the carbon materials prepared from the BZ/PhRs composites.

Table 1. BET surface area and surface atomic composition of the prepared carbon

Sample	S_{BET} /m^2 g^{-1}	Atomic ratio (XPS)		
		B/C	N/C	O/C
PhRs	265	0	0	0.08
BZ/PhRs10	292	0	0	0.18
BZ/PhRs30	302	0.01	0	0.20
BZ/PhRs50	190	0.06	0.01	0.16

Figure 3. C1s, B1s, and O1s XPS spectra of the prepared carbon, dots: measured data; lines: fitted curves.

proposed molecular structure. The carbonized residue (char yield) of the compound **3** was more than 38% at 800 °C in nitrogen atmosphere.

The borazine compound was mixed with phenolic resin (PhRs; Gunei Chemical, PSK-2320) in various ratios, using ethyl acetate as a solvent. After the solvent was removed, the mixture was pyrolyzed under a flow of inert gas at 1000 °C for 5 h, and the obtained carbon materials were abbreviated as BZ/PhRsXX, where XX represents the weight percent of BZ in the precursor.

The specific surface area was determined by N$_2$ adsorption using a volumetric adsorption measurement instrument (Bel Japan, Belsorp-mini II). X-ray photoelectron spectroscopy (XPS) was carried out using a spectrometer equipped (JPS-9010MC, JEOL) with a monochromator with an Al anode at 12 kV and 25 mA. The binding energy was charge corrected with respect to the C1s signal at 289.3 eV derived from carboxy groups.[14] This charge correction was double-checked with respect to the C1s signal at 284.6 eV from aromatic carbons[15] after peak deconvolution. Peak deconvolution was carried out by utilizing the Voigt function. X-ray diffraction (XRD) was measured at room temperature using an X-ray diffractometer (Rigaku, Ultima IV) with Cu Kα radiation.

Figure 2 shows the XRD patterns of the carbon materials BZ/PhRsXX. In all spectra, broad diffraction peaks due to the (002) plane of turbostrutic carbon were observed at around 24.4°. The degree of graphitization does not seem to depend on the amount of BZ in the composites. The BET surface area determined by N$_2$ adsorption and the surface composition determined by XPS are summarized in Table 1. A small amount of BZ addition (10–30%) does not change the specific surface area; however, BZ/PhRs50 has lower specific surface area than the other three, which is not ideal for electrocatalysis. As to the surface compositions, the addition of BZ increased boron content but did not affect the nitrogen content in the resulting carbon. BZ/PhRs50 has the highest boron content, B/C = 0.06, in the present carbons. This value is much higher than a reference in the previously reported studies. Ozaki et al. used BF$_3$–MeOH complex as the boron source and resulted in quite low boron content after pyrolysis in spite of an excess amount of

the boron source in the precursor (B/C = 0.38).[12b] It can be concluded that our new precursor, BZ, is a good boron dopant for carbon materials. In addition, it should be noted that the oxygen content of the BZ/PhRs samples increased compared to that of the PhRs sample.

Detailed XPS study was carried out to clarify the surface species introduced onto the present carbons. Figure 3 shows the C1s, B1s, and O1s XPS spectra of the PhRs, BZ/PhRs30, and BZ/PhRs50. All signal intensity was normalized with respect to the total area count of each C1s spectrum. The C1s spectra were deconvoluted into four peaks: aromatic carbon at 284.6 eV, ether (C*OC) species at 285.6–285.7 eV, ester (C*OC=O) species at 286.9–287.0 eV, and carboxy (C*(=O)O) species at 289.3 eV.[14] The B1s spectra were deconvoluted into four peaks: BC$_3$ moiety at 189.5 eV, BC$_2$O moiety at 190.9 eV, BCO$_2$ moiety at 191.8–192.0 eV, and B–O bonds at 193.0 eV.[12b] The O1s spectra were deconvoluted into four peaks: carbonyl (C=O*) species at 531.4–531.5 eV, ether (CO*C) species at 532.5–532.6 eV, ester
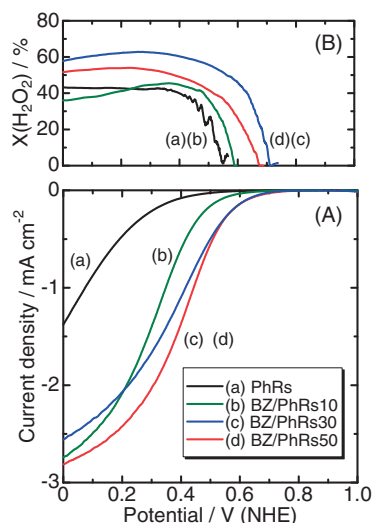
Figure 4. (A) ORR voltammograms and (B) H_2O_2 selectivity with the prepared catalysts. $T = 25\,°C$, electrolyte: 0.5 M H_2SO_4, catalyst loading: $0.2\,mg\,cm^{-2}$, rotation: 1500 rpm.

($CO^*C{=}O$) species at 533.4–533.6 eV, and carboxylic acid (COOH) at 534.2–534.3 eV.[16] These XPS spectra clearly suggest that many oxygen functionalities were introduced into the BZ derived samples. However, it is not quite clear by what kind of mechanism the boron species affect the oxygen content of the carbon materials. The boron and oxygen might locate quite close to each other such as B–C–O moiety or the boron species might have worked as a catalyst to introduce oxygen species during the pyrolysis step.

Figure 4A shows the ORR voltammograms measured in 0.5 M H_2SO_4 with the catalysts fabricated under various BZ ratios. While the carbon material derived from only PhRs shows quite poor ORR activity, the catalysts from BZ/PhRs clearly show better ORR performances. These ORR catalytic activities are much better than the previously reported BN-doped catalysts. For instance, the current density at 0.4 V is $1.37\,mA\,cm^{-2}$ for the BZ/PhRs50, whereas the BN3 catalyst by Ozaki et al. shows below $0.19\,mA\,cm^{-2}$, in a similar experimental setup and the same catalyst loading.[12] Figure 4B shows approximately 50% of selectivity to H_2O_2 via two-electron pathway under this experimental condition. This peroxide selectivity is too high to consider the present version of catalysts for the PEMFC applications. However, if one designs an ORR catalyst based on $2 + 2$ electron pathway,[17] two-electron electrochemical reduction to H_2O_2 followed by another two-electron electrochemical reduction to H_2O, this type of material could be a good catalyst for the first two-electron reduction.

There are several explanations for the origin of the ORR activity over the BZ/PhRs-derived samples. One convincing explanation is that the quinone/hydroquinone redox couple catalyzes the ORR over the BZ/PhRs-derived carbon.[18] It is quite clear from the present experimental results that the BZ addition to PhRs introduces a large amount of oxygen-containing functional groups. Otherwise, boron species incorporated in carbon lattice might enhance oxygen adsorption onto the carbon surface and result in the improved ORR activity. One might assume that a B–N–C moiety is responsible for ORR as Ozaki

et al. proposed; however, it is not likely the case in the present class of carbon since the nitrogen content in the prepared carbon is extremely low.

In conclusion, BZ has been successfully synthesized and works as a good precursor for introducing boron and oxygen species into carbon materials. The XPS results clearly suggest that the carbon material with high boron and oxygen contents has been prepared from a new borazine with phenolic resin dopant. The oxygen reduction catalytic activity is much improved by the addition of this precursor. Further study must be done to specify what kind of chemical structures are responsible for which reaction pathways of ORR.

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19　Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.