Heteroatom-Doped Carbon as a Non-precious Catalyst for Oxygen Reduction Reaction in Alkaline Medium

Gayoung Jo (조 가 영 佳 英)

Department of Energy Systems Engineering

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Advisor: Professor Sangaraju Shanmugam

Co-advisor: Doctor Soonhyun Kim

by

Gayoung Jo

Department of Energy Systems Engineering
DGIST

A thesis submitted to the faculty of DGIST in partial fulfillment of the requirements for the degree of Master of Science in the Department of Energy Systems Engineering. The study was conducted in accordance with Code of Research Ethics

12. 05. 2012

Approved by

Professor Sangaraju Shanmugam (Signature)
(Advisor)

Doctor Soonhyun Kim (Signature)
(Co-Advisor)

1 Declaration of Ethical Conduct in Research: I, as a graduate student of DGIST, hereby declare that I have not committed any acts that may damage the credibility of my research. These include, but are not limited to: falsification, thesis written by someone else, distortion of research findings or plagiarism. I affirm that my thesis contains honest conclusions based on my own careful research under the guidance of my thesis advisor.
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Accepted in partial fulfillment of the requirements for the degree of Master of Science.

12. 05. 2012

Head of Committee

Prof. Sangaraju Shanmugam

Committee Member

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Committee Member

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Abstract

A facile and cost-effective single-step pyrolysis approach using a single precursor is introduced to fabricate boron-doped carbons (BDC700 and BDC900) and phosphorus or boron selective-doped-graphenes (PDG700 and BDG900) without using a template, solvent, or catalyst. By increasing the temperature from 700 °C to 900 °C, the tuning of the boron doping level was found in BDCs, and tuning of doping level and selection of heteroatom were possible in PDG700 and BDG900. BDC900, PDG700, and BDG900 were found to have the ability to reduce oxygen directly to water with a four-electron oxygen reduction pathway in an alkaline medium. All four catalysts exhibited excellent stability and resistance to methanol oxidation and CO poisoning. BDCs, PDG700, and BDG900 are a promising alternative to conventional Pt-based catalysts as metal-free catalysts for oxygen reduction reaction in alkaline fuel cells.

Keywords: Heteroatom-doped carbon, Electrocatalyst, Oxygen reduction, Alkaline fuel cells, Non-precious catalyst
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I. Introduction

1.1 Motivation

Conventional fossil fuel energy sources, such as petroleum, natural gas, and coal, which meet most of the world’s energy demand, are being depleted at faster rate than the world’s population is increasing. Their combustion products also are causing global climate problems, such as the greenhouse effect and air pollution. Therefore, the focus has shifted towards environmentally friendly and renewable energy production systems, such as solar cells, wind turbines, and fuel cells. Especially, the environment-friendly features and high efficiency of fuel cells have been attracting enormous interest among researchers.

The fuel cell is a promising alternative energy conversion device that converts chemical energy to electrical energy directly and efficiently with water from the reaction between hydrogen and oxygen. Fuel cells are categorized based on the type of electrolytes used and their operating temperature. Examples include: (1) polymer electrolyte membrane fuel cells (PEMFCs), (2) alkaline fuel cells (AFCs), (3) phosphoric acid fuel cells (PAFCs), (4) molten carbonate fuel cells (MCFCs), and (5) solid oxide fuel cells (SOFCs). In particular, PEMFC is one of the most actively investigated fields owing to its low operation temperature and portable application. The single cell of PEMFCs consists of membrane electrode assembly (MEA) and gas channels. The MEA is made of two gas diffusion layers (GDLs), two carbon supported catalyst layers (CLs), and PEM. In CLs, hydrogen oxidation reaction (HOR) and oxidation reduction reaction (ORR) occur at anode and cathode, respectively. Between two electrode reactions, ORR is sluggish and considered as a barrier for commercialization of the fuel cell. To improve ORR kinetics, high platinum (Pt) loading is necessary, which results in the high cost of fuel cell electrode catalyst.

Fuel cell electrodes account for 33% of the whole cost of fuel cells. To use less Pt in the cathode is one way to reduce the overall cost of the fuel cell. Thus, non-precious catalysts should be
researched and developed to overcome the high costs of fuel cells.

An alkaline polymer electrolyte membrane fuel cell (APEFC) is a counterpart of PEMFC that uses an alkaline electrolyte. It uses non-precious catalysts owing to its faster ORR kinetics and better stability of electrode materials under alkaline conditions. For these reasons, this study focused on the development of non-precious catalysts for the ORR.

In recent years, heteroatom (N, B, and P) doped carbons have received enormous importance as a non-precious-metal electrode materials for oxygen reduction. Doping of heteroatom into a carbon network can be mainly conducted by (1) intercalation and (2) substitution. Particularly, substitutional doping of heteroatom into carbon is able to modify the electronic properties of the carbon network, and accordingly tune the electrocatalytic activities.

To substitute heteroatom into the carbon network, three methods have been mainly reported: (1) arc-discharge method, (2) laser-ablation method, and (3) chemical vapor deposition (CVD). These techniques allow high energy consumption, expensive hardware and multistep processes, which lead to a costly manufacturing process. On the other hand, solid-state pyrolysis is a simple and facile single-step synthetic approach to prepare heteroatom doped carbon. The synthetic approach has been considered as a green process because it does not use templates, solvents, or catalysts. In addition, this process can be easily up-scaled.

Boron doping into a carbon network leads the host graphitic carbon array to have p-type conductivity and play the role of electron acceptor due to the strong electron withdrawing capability at the hexagonal site. Phosphorus doping into a carbon network is the counterpart of boron-doped carbon, which makes the host carbon array have n-type conductivity. Although nitrogen-doped carbon materials have been widely investigated for ORR kinetics, a few reports emphasized the use of phosphorus or boron-doped carbon based catalysts for fuel cell ORRs in the field of fuel cells.
1.2 Objectives

The objectives of this study are

- To introduce a facile and cost-effective solid-state pyrolysis to prepare boron-doped carbon (BDCs) and phosphorus or boron-selective-doped graphene (PDG700 and BDG900) as non-precious and metal-free catalyst for alkaline fuel cells.
- To fabricate heteroatom-doped carbons to have comparable ability to reduce oxygen with commercial Pt-based catalysts and outstanding stability under continuous oxygen reduction, the presence of CO gases and methanol.
- To decrease the overall cost of fuel cell production by replacing high-priced Pt catalysts with non-precious catalysts.
II. Theoretical background

2.1 Fuel cells

2.1.1 Fuel cells fundamentals

1) Basic principle of fuel cells

Fuel cells are energy devices that convert chemical energy of hydrogen fuel and oxidant into electricity. In this process, water and heat are also generated as by-products. In a fuel cell, the reverse of water electrolysis is the main chemical reaction for generating electricity. Figure 2-1 depicts the general concept of fuel cells using $\text{H}_2$ as a fuel and $\text{O}_2$ as an oxidant.

![Figure 2-1. General concept of $\text{H}_2/\text{O}_2$ fuel cells.](image)

The single unit of fuel cells, called the single cell, consists of a membrane-electrode assembly (MEA) and a gas diffusion layer (GDL). The MEA includes a membrane and two electrodes that consist of anode and cathode. In the electrode, a hydrogen oxidation reaction (HOR) and an oxygen reduction reaction (ORR) occur in the anode and cathode, respectively. In fuel cells using acidic electrolyte, electrons and protons ($\text{H}^+$) are generated during HOR. The electrons move towards the cathode through an external circuit and generate electrical current. At the same time, the protons
(H⁺) penetrate through the membrane electrolyte. Once the electrons and the protons are delivered to the cathode, oxygen is reduced to water (H₂O).² In fuel cells using alkaline electrolyte, HOR starts with consuming a hydroxide ion (OH⁻) of electrolyte, and water and electrons are generated. The electrons generated on the anode side contribute to ORR in the cathode. With ORR in alkaline medium, hydroxide ions are formed, and the hydroxide ion moves toward the anode side via the electrolyte.²⁹,³⁰ In both types of fuel cell, water as a by-product must be removed because if it remains in the fuel cell, it can degrade performance.³¹

![Electrode reactions in (a) acidic and (b) alkaline electrolytes.](image)

**Figure 2-2.** Electrode reactions in (a) acidic and (b) alkaline electrolytes.

Heat by-products are released from the energy difference between water bonding configuration and initial hydrogen/oxygen bonding configuration.³²

The single fuel cell generates a little amount of direct current (DC) electricity; thus, several single cells are assembled together in a stack for actual applications. The operation and principle of single cells and stacks are the same.²,³²
2) Operation of fuel cells

R. O’hayre et al.\textsuperscript{32} defined the operation of fuel cells into the four steps shown in Figure 2-3: These four steps are: (1) Reactant delivery (transport) into the fuel cell, (2) Electrochemical reaction, (3) Ionic conduction through the electrolyte and electron conduction through the external circuit, and (4) product removal from the fuel cell.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fuel_cell_diagram}
\caption{Cross-section of fuel cell illustrating major steps for generating electricity: (1) reactant transport, (2) electrochemical reaction, (3) ionic and electronic conduction, and (4) product removal.\textsuperscript{32}}
\end{figure}

To generate electricity, fuel cells require continuous supply of fuel and oxidant into the anode and cathode, respectively. An insufficient supply of reactant can lower fuel cell performance. (Step 1: Reactant transport) Fuel and oxidant are reactants for further electrochemical reactions. Once fuel and oxidant reach each electrode after flowing through flow field plates, the electrochemical reactions (HOR and ORR) occur on the surface of the three phase interface between catalysts, electrolyte and reactants in the electrode.\textsuperscript{33} The current generated by electron flow correlates with the electrochemical reaction rate. The faster the electrochemical reaction, the higher current produced, and vice versa. For the higher current, catalysts are required to enhance the electrochemical reaction rate. (Step 2: Electrochemical reaction) Electrons and ions are formed during the electrode reactions. The
electrons move through the external circuit from the anode to the cathode while generating electricity. At the same time, the ions should be conducted through the electrolyte membrane because the ions produced at one electrode have to be consumed at the other electrode. (*Step 3: Ionic and electronic conduction*) All fuel cell electrode reactions generate by-product that should be removed. For example, H₂/O₂ fuel cells generate water, while hydrocarbon fuel cells generate water and carbon dioxide. These by-products interrupt the reactants to attend the electrode reactions. Often, product removal is a minor problem in fuel cells operated under high temperature. However, low temperature fuel cells, such as PEMFCs and AFCs, have been suffered from performance degradation due to remaining products if the operating temperature is lower than the boiling point of water. Yi et al.³¹ reported the presence of liquid water formed from saturated vapor below the boiling point of water can cause mass-transport limitations resulting from the “the restriction of oxygen transport through the gas-diffusion electrode and flooding of active catalyst sites, especially at high current density.” In addition, the presence of water within the GDL and/or gas flow field can cause a non-uniform distribution of reactants over the active catalyst area and among single cells in a stack. This phenomenon results in poor cell performance and cell-to-cell performance variation within a stack. Thus, product removal is critical issue for efficient fuel cell operation. (*Step 4: Product removal*)

![Figure 2-4. Basic structure of electrode and flow of reactant and product.](image)
3) Performance of fuel cells

The performance of fuel cells can be summarized by a polarization curve ($i-V$ curve). The $i-V$ curve shows the voltage output of fuel cells for a given current input. By using the $i-V$ curve, a power density curve, shown in Figure 2-5, can be drawn by multiplying the voltage at each point by the corresponding current density. The power density is the amount of power generated from fuel cells per unit area of the electrode; furthermore, the value is one criterion to evaluate a single cell or stacks.

$$P = iV$$

(2.1)

![Figure 2-5. A typical fuel cell polarization curve obtained from the diagnostic modeling. PEM fuel cell with an active area of 192 cm$^2$, designed by NRC-IICL.](image)

In ideal fuel cells, if reactants are supplied sufficiently, voltage is maintained constantly while current is generated by thermodynamics. Unfortunately, in practice, to maintain high voltage is difficult under current load. As shown in Figure 2-6, the voltage output of actual fuel cells is less than that of thermodynamically ideal fuel cells due to three major irreversible losses, which is called overpotential: (1) activation losses, (2) ohmic losses, and (3) concentration losses. Therefore, the actual voltage output can be defined by the following equation that thermodynamically predicts voltage output is subtracted by three voltage losses.
\[ V_{\text{act}} = E_{\text{thermo}} - \eta_{\text{act}} - \eta_{\text{ohmic}} - \eta_{\text{conc}} \quad (2.2) \]

where \( V_{\text{act}} \) is real output voltage, \( E_{\text{thermo}} \) is thermodynamically predicted voltage output, \( \eta_{\text{act}} \) is activation losses, also called charge-transfer losses, \( \eta_{\text{ohmic}} \) is ohmic losses, and \( \eta_{\text{conc}} \) is concentration losses.

Figure 2-6. Typical schematic of fuel cells voltage/current characteristics.\(^3\)

The main reason of activation loss is kinetics of electrochemical reaction occurring in the electrodes; in addition, electrocatalyst material, reactants activities, and current density can affect the losses. To alleviate the losses, effective catalysts are needed to enhance the kinetics of the electrode reactions. The ohmic loss, called IR drops, is due to ionic resistance between electrode and electrolyte, electronic resistance in electrodes, and resistance in current collector and interconnects. To decrease the losses, the use of low resistance material and optimization of MEA thickness can be solutions. The concentration loss is owing to finite mass transport limitation rates of reactants. Furthermore, the loss strongly depends on current density, reactants activities, and electrode structure. In fuel cells, insufficient \( \text{O}_2 \) gas supply is also one reason; thus, if \( \text{O}_2 \) gases are provided constantly and sufficiently, the concentration losses are can be lowered.
Figure 2-7 shows polarization contribution of two half cells for phosphoric acid fuel cells (PAFCs). Clearly, polarization contribution of the cathode is four to five times higher in both O\textsubscript{2} and air atmosphere than that of the anode. This difference between two electrodes means that the decrease in polarization, equal to ‘overpotential’ and ‘loss’, of cathode side is critical issue to decline overall voltage losses and to enhance voltage output in fuel cells. The shape of the graph is common with other kinds of fuel cells as well.

![Figure 2-7. Contribution of anode and cathode voltage loss to polarization.](image)

4) Types of fuel cells

For now, there are five types of fuel cells that are possible or close to commercialization.\textsuperscript{3,5,35} Generally, types of fuel cells are classified according to operating temperature, application, and electrolyte used. Table 2-1 presents fundamental information of the five types of fuel cells.
Table 2-1. Types of fuel cells

<table>
<thead>
<tr>
<th></th>
<th>PEMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrolyte</strong></td>
<td>Polymer membrane</td>
<td>Polymer/liquid membrane</td>
<td>Phosphoric acid</td>
<td>Molten carbonate salt</td>
<td>Solid electrolyte</td>
</tr>
<tr>
<td></td>
<td>(PFSA)</td>
<td>(KOH)</td>
<td>(H₃PO₄)</td>
<td>((Li, K)₂CO₃)</td>
<td>(ZrO₂)</td>
</tr>
<tr>
<td><strong>Mobile Ion</strong></td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>CO₃²⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td><strong>Operating Temperature</strong></td>
<td>30~100 °C</td>
<td>50~200 °C</td>
<td>190~220 °C</td>
<td>650 °C</td>
<td>500~1000 °C</td>
</tr>
<tr>
<td><strong>Fuel(s)</strong></td>
<td>H₂</td>
<td>H₂</td>
<td>H₂</td>
<td>H₂, CO, CH₄</td>
<td>H₂, CO, CH₄</td>
</tr>
<tr>
<td><strong>Oxidant</strong></td>
<td>O₂, air</td>
<td>O₂, air</td>
<td>O₂, air</td>
<td>CO₂, O₂, air</td>
<td>O₂, air</td>
</tr>
<tr>
<td><strong>Efficiency</strong></td>
<td>40~60%</td>
<td>45~60%</td>
<td>35~40%</td>
<td>45~60%</td>
<td>50~65%</td>
</tr>
<tr>
<td><strong>Applications</strong></td>
<td>Vehicles, mobile phones</td>
<td>Submarines, spacecraft</td>
<td>Power stations</td>
<td>Power stations</td>
<td>Power stations</td>
</tr>
</tbody>
</table>
2.1.2 Oxygen reduction reaction (ORR)

1) Mechanism of oxygen reduction reaction (ORR)

Electrochemical oxygen reduction reaction occurring in cathode electrode of fuel cells occurs mainly by two pathways in aqueous solution. One is four-electron pathway generating water (H₂O) from oxygen (O₂); the other is two-electron pathway forming hydrogen peroxide (H₂O₂) from oxygen (O₂) as a product. Table 2-2 describes the mechanism of ORR in two types of acidic and alkaline aqueous solution. The acidic and alkaline medium correspond to electrolyte of PEMFCs/PAFCs and AFCs, respectively.

Table 2-2. Thermodynamic electrode potential of electrochemical ORR$^{34,36,37}$

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>ORR reactions</th>
<th>Thermodynamic electrode potential at standard conditions, V vs. SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic aqueous solution</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{H}_2\text{O}$</td>
<td>1.229</td>
</tr>
<tr>
<td></td>
<td>$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>1.76</td>
</tr>
<tr>
<td>Alkaline aqueous solution</td>
<td>$\text{O}_2 + \text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$</td>
<td>0.401</td>
</tr>
<tr>
<td></td>
<td>$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$</td>
<td>-0.065</td>
</tr>
<tr>
<td></td>
<td>$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^-$</td>
<td>0.867</td>
</tr>
</tbody>
</table>

In fuel cells, 4-electrons pathway of ORR is strongly preferred generally. Two-electron pathway decreases the overall cell potential in some fuel cells including alkaline fuel cells; in addition, H₂O₂ produced by two-electron pathway accelerates degradation of membrane and catalysts due to oxidizing by H₂O₂. On the other hand, some fuel cells use H₂O₂ as oxidant instead of O₂. $^{38,39}$
2) Kinetics of oxygen reduction reaction (ORR)

(1) Limiting current density

The ORR limiting current \( (i_L) \) at the RDE can be expressed by Levich equation (Eq. 2.3):\(^{36,40}\)

\[
i_L = 0.62 \, nFAC_bD_0^{2/3}v^{1/6}\omega^{1/2}
\]

(2.3)

where \( n \) is the electron transfer number, \( F \) is the Faraday constant (96485 C mol\(^{-1}\)), \( A \) is the geometric surface area of the RDE, \( C_b \) or \( C_{O_2} \) is the the bulk concentration of \( O_2 \) (1.2 x 10\(^{-3}\) molL\(^{-1}\)), \( D_0 \) is the diffusion coefficient of \( O_2 \) (in 0.1 M KOH: 1.9 x 10\(^{-5}\) cm\(^2\)s\(^{-1}\)), \( v \) is the kinematic viscosity (0.1 M KOH: 0.01 cm\(^2\)s\(^{-1}\)), and \( \omega \) is the rotating speed of the disk (rpm).

From the above equation, the linear dependence of \( i_L \) on \( \omega^{1/2} \) is found with a zero intercept shown in Figure 2-8. A slope, equal to \( 0.62 \, nFAC_bD_0^{2/3}v^{1/6} \), is proportional to the number of electrons (n) transferred per \( O_2 \) molecule.

A Levich plot, plotted \( j_L \) as functional of \( \omega^{1/2} \), suggests that the ORR is controlled by the diffusion of \( O_2 \) to the electrode if the plot is close to being straight.\(^{40}\)

Theoretically, if electron transfer number is four, \( i_L \) should be -5.7 mAcm\(^{-2}\) at an electrode rotation rate of 1600 rpm in an electrolyte of 0.1 M KOH aqueous solution.
(2) Koutekey-Levich (K-L) plots for the ORR

A Koutekey-Levich (K-L) equation and a plot is an effective and powerful tool to investigate kinetic aspects of oxygen reduction. K-L equation is given in Eq. 2.4:\textsuperscript{3,36}

\[
\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_k} \quad (2.4)
\]

where \(J\) is the measured current density, \(J_L\) is the diffusion-limiting current density, \(J_k\) is the kinetic current density, and \(B\) is equal to \(0.62 \ nFAC_bD_0^{2/3}v^{-1/6}\). K-L plot is plotted \(j^1\) as functional of \(\omega^{1/2}\). In the K-L plot, a slope and y-intercept should be \(B^{-1}\) and \(J_k^{-1}\). Therefore, electron transfer number (n) can be calculated from the slope by Eq. 2.5, and kinetic current density (\(J_k\)) can be obtained from the y-intercept of the plot. Theoretically, the slope of the K-L plot should be 4.54 and 2.27 if the ORR follows two-electron and four-electron pathway, respectively.

\[
\frac{1}{\text{slope}} = B
\]

\[
n = \frac{B}{0.62F(D_0)^{2/3}v^{-1/6}(CO_2)} \quad (2.5)
\]

The linearity and parallelism of a K-L plot indicates that the ORR follows a first-order kinetic. Furthermore, the parallelism, constant slope, of the lines plotted at various potential means constant electron transfer number and the reaction order over various potential ranges.\textsuperscript{40}

The K-L plot can be drawn by using hydrodynamic voltammograms obtained by RDE.
Figure 2-8. (a) Hydrodynamic voltammograms obtained in (0) N₂- and (1-7) O₂-saturated 0.5 M H₂SO₄ solution with increasing electrode rotation speeds, (b) Levich plot for the ORR at the Au (poly) RDE in O₂-saturated 0.5 M H₂SO₄, and (c) K-L plots for the ORR in O₂-saturated 0.5 M H₂SO₄ at the Au (poly) RDE reported by Miah et al.⁴⁰
2.2 Heteroatom-doped carbon

2.2.1 Properties

1) Boron-doped carbon

Boron is a chemical element having atomic number of five. Electronic properties of boron come from electron configuration and valence electrons. One fewer valence electron of boron (three electrons) than that of carbon atom (four electrons) donates a hole resulting p-type conductivity in boron-doped carbon. In other words, doped boron acts as both electron acceptor and hole donator at the hexagonal site due to one fewer valence electron. It is also owing to a shift of the Fermi level from center of band gap to the valence band. This electronic modification by doping boron can contribute to enhance electrocatalytic activities to the intrinsic carbon.

The strong electron withdrawing capability of doped boron induces adsorption of O\textsubscript{2} molecular on the doped boron. Yang and coworkers\textsuperscript{12} also illustrated that O\textsubscript{2} adsorption is favorable on boron dopant rather than adjacent carbon atoms by more positive charged boron atom than carbon atom\textsuperscript{43,44} due to lower electronegativity of boron (2.0) than that of carbon atom (2.5).\textsuperscript{45} O\textsubscript{2} adsorption is important step for further steps for the oxygen reduction.\textsuperscript{46}

Endo et al.\textsuperscript{26} reported electronic structure on the surface of boron-doped highly oriented pyrolytic graphite (HOPG) by using scanning tunneling microscopy (STM). In Figure 2-9, the STM image of B-doped HOPG depicts that mottled bright areas show an inhomogeneous electron density in the base plane of B-doped HOPG due to boron doping, while a pristine HOPG displays homogeneous electron density. In Figure 2-9 (b), doped boron and neighbor six carbons are observed at the brightest site and at medium bright sites, respectively. Inequality of brightness indicates localized electron density distribution on the boron-doped areas. That is, the doped boron atoms affect the electronic structure and electron distribution of the adjacent six carbon atoms.
Figure 2-9. Net charges for each atom in the BC₃H₉ molecule. B: pink, C: dark gray, and H: gray.¹²

Figure 2-10. STM images of a three-dimensional surface plot and section analysis corresponding to the line indicated (see the insets) of (a) the HOPG and (b) B-doped HOPG graphene surfaces.²⁶
2) Phosphorus-doped carbon

Phosphorus is a chemical element having atomic number of fifteen and belongs to same group as nitrogen. Unlike boron atom, one more valence electron of phosphorus (five electrons) than that of carbon atom (four electrons) supply a electron that cause n-type conductivity in phosphorus-doped carbon.\(^4^7\) For this reason, doped phosphorus that is n-type conductor plays a role of both electron donor and hole acceptor at the hexagonal site. This electronic properties of phosphorus-doped carbon can be explained by a shift of the Fermi level from center of band gap to the conducting band.\(^4^2\) This electronic modification by doping phosphorus can improve electrocatalytic activities to the intrinsic carbon materials.

Liu et al.\(^8\) reported net charge of phosphorus doped carbon by using quantum mechanics calculations. In Figure 2-11, dope phosphorus has more positive charge (+0.652) than neighbor carbon atom that is induced to relative negative charge (-0.298). Yu et al.\(^4^8\) also suggested that doped phosphorus creates more positive charge than the parent carbon atom. This calculation indicates that \(\text{O}_2\) adsorption is favorable on phosphorus atom in phosphorus doped-carbon, which is same tendency as doped boron atom into the carbon network. This tendency may be due to lower electronegativity of phosphorus \((2.1)^{4^5}\) than that of carbon \((2.5)\) even though electron configuration and number of valence electron of phosphorus is same as nitrogen atom.
Figure 2-11. Net charge for some selected atoms of the H-terminated graphene sheet in its optimized structures. (a) The ideal (pure) graphene sheet, (b) graphene sheet with one phosphorus atom. P: yellow, C: dark gray, and H: gray.
2.2.2 Synthetic approaches

1) Arc-discharge method

Arc-discharge (Electric arc) is a type of electrical conduction in gases characterized by high current density and low potential drop.\(^{19,49}\) B-doped carbon is produced when BN/graphite or B/graphite is arced in an inert atmosphere such as He, N\(_2\) at low pressure.\(^{17}\) In the same manner, P-doped carbon can be fabricated by using PN/graphite or P/graphite. Apparatus for the method consists of two carbon rods placed end to end of the apparatus, separated by approximately 1 mm.

The arc-discharge method is the most common and the easiest way to dope heteroatom into the carbon network; however, it has several problems.\(^{17}\) (1) Products contain a mixture of target materials and impurities that consist of soot and catalytic metals. Thus, additional purification is needed to remove the impurities. (2) Occasionally, ill-formed structures are formed as shown in Figure 2-12.

![Figure 2-12](image)

**Figure 2-12.** (a) TEM image of B-doped carbon nanotubes produced by the arc-discharge technique. Note that the amount of polyhedral particles is significantly reduced; (b–c) HRTEM images of ill-formed nanotube caps showing irregular closings of the tube ends; note the amorphous material around the tip in (b).\(^{21}\)
2) Laser-ablation method

Laser ablation is a method of producing nano-scaled structures from a precursor (solid or liquid) surface by irradiating it with a laser beam.\textsuperscript{22,23} High-power laser pulses are required to evaporate the material from the precursor such as ‘B or P-graphite-Co-Ni’ or ‘BN or PN-graphite-Co-Ni’ for preparing B or P-doped carbon, and then vaporized precursor gathers on the surface of the cooled collector.\textsuperscript{17}

The method is simple and applicable to many aspects. In particular, lattice defects and impurities can be minimized because chemicals such as solvent are unnecessary. However, additional catalyst is required for the laser ablation; hence, final products containing only boron cannot be obtained without additional purification processes.\textsuperscript{50}

3) Chemical vaporization deposition (CVD)

Chemical vaporization deposition (CVD) is the process of vaporizing volatile precursors, which react and/or decompose on the surface of catalytic metal deposited on substrate (e.g., Si(100)) The nano-scaled catalytic metal is formed after additional etching step using NH\textsubscript{3} gas at 750 °C to 1050 °C. B-doped carbon synthesizes on the catalytic metal particles. Fe, Ni, Co, or an alloy of the three metals is used as the catalysts.\textsuperscript{17}

Frequently, volatile by-products are also produced. They should be removed by inert gas flow through the reaction chamber.

This method can be used with precursors having a high melting point at a lower temperature than the melting point. Also, mass production is possible by this method, however, additional catalysts are required;\textsuperscript{24,25} in addition, the design of CVD systems is difficult and complicated. Another problem is the use of harmful and combustible gases such as NH\textsubscript{3}. 

- 21 -
4) Pyrolysis

Pyrolysis is a chemical change in which organic materials decompose in a furnace, below 1000 °C, in the absence of oxygen; in other words, it corresponds to thermolysis of organic materials. Thermolysis (thermal decomposition) is conducted by using the arc-discharge, laser ablation, or CVD, which are multistep processes. On the other hand, pyrolysis can be conducted by a single step without gases such as carriers and etchers. Occasionally, inert atmosphere is required to carry precursors or to stabilize atmosphere in the furnace.

After organic precursors containing boron or phosphorus are put into the center of the furnace, and then temperature is elevated, B or P-doped carbon is formed as the chemical bonds of the precursor break and reorganize.

In particular, solid-state pyrolysis, which uses solid-state precursor, is one promising approach to synthesize heteroatom-doped carbon due to its simplicity and easy up-scaling. In addition, the use of templates, solvents, or catalysts are not mandatory. Often, the heteroatom-doped carbon is synthesized by using a single precursor containing both target heteroatom and carbon. The use of a single precursor and the lack of a template, solvent, or catalysts can simplify the synthetic process and reduce production costs.

2.3 Graphene

Graphene, a monolayer of graphite, has been drawing much attention as a promising electrode material due to its unique electronic properties. In addition, the outstanding mechanical and thermal properties of graphene can be considered for various areas.
2.3.1 Properties

1) Morphology and structure

Graphene has a hexagonal lattice that is composed of two equivalent sub-lattices of carbon atoms. In the carbon atoms of graphene, three electrons among four peripheral electrons of carbon form strong covalent bond; thus, graphene consists of planar hexagonal net. The remaining one peripheral electron exists perpendicularly to the graphene plane.\textsuperscript{51} The electronic state derived from the covalent bonded three electrons is defined as $\sigma$-orbital. That is, the carbon atoms of the graphene are bonded together with $\sigma$ bonds as shown in Figure 2-13 (a) and (b). On the other hand, the electronic state from an electron having perpendicular direction to the graphene is equal to $\pi$-orbital.\textsuperscript{52} The $\pi$-orbital of conjugated electrons of the graphene contribute to electronic conduction.\textsuperscript{53}

TEM study, shown in Figure 2-13 (c), shows sheet-like shape of the graphene.

\textbf{Figure 2-13.} (a) Graphene structure of a single two-dimensional hexagonal sheet of carbon atoms,\textsuperscript{51} (b) Schematic of the in-plane $\sigma$ bonds and the $\pi$ orbitals perpendicular to the plane of the graphene sheets,\textsuperscript{51} and (c) TEM image of graphene sheet.
2) Electronic properties

The electronic properties of graphene are due to the unique energy band structure shown in Figure 2-x. Intrinsic graphene is a zero-gap semiconductor; thus, graphene is also called a semi-metal. The electronic-band structure of graphene is a combination of semiconducting and metallic characteristics as vanishing bandgap ($E_g$) and Fermi surface, respectively.$^{54}$

Tunable band gap and partial defects derived from sp$^3$-carbon of graphene are also unique electronic properties of the graphene. In addition, the graphene has a high mobility of charge carriers up to $105 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

![Figure 2.14](image)

**Figure 2.14.** Electronic band structure. (a) Band structure of graphene and (b) The linear dispersion relation showing the vertically mirrored Dirac cones intersecting at the Fermi energy, $E_F$. $^{53}$

3) Mechanical, thermal and other properties

The mechanical strength of graphene is stronger than any other materials. Lee et al.$^{55}$ reported that suspended graphene exhibited a mechanical strength of 53 Gpa. On the other hand, graphene also has high elasticity due to its the hexagonal structure with a Young’s modulus of 1 Tpa, elastic stiffness of 2 TPa$^{56}$, and a shear modulus of 280 Gpa.$^{56}$

Thermally, graphene is very stable under high temperature, and its temperature limitation is yet to be found.$^{53}$ The thermal conductivity of graphene is also as high as $5 \times 10^3 \, \text{Wm}^{-1}\text{K}^{-1}$.$^{57}$
Furthermore, graphene shows a very high surface area (2600 m$^2$g$^{-1}$) in comparison with graphite (10 m$^2$g$^{-1}$) and carbon nanotubes (1300 m$^2$g$^{-1}$).\textsuperscript{58} A large surface area of catalyst materials can provide a huge amount of sites where reactants are adsorbed for further catalytic reactions.

### 2.3.2 Applications

Electrochemically, promising applications of graphene are graphene field emission, gas and biosensors, field effect transistors (FET), transparent electrode, electrochemical energy conversion, and electrocatalysis.\textsuperscript{51,59}

In particular, electrocatalysis and energy conversion applications have been considered for applications to electrode materials of clean energy devices, such as Li-based secondary batteries (LIB),\textsuperscript{60,61} solar cells,\textsuperscript{62,63} supercapacitors/ultracapacitors\textsuperscript{64,65}, and fuel cells.\textsuperscript{13,14,66} This consideration is due to superior electrical conductivities, high surface area, chemical tolerance, high transparency, and a broad electrochemical window.\textsuperscript{59}
III. Experimental

3.1 Preparation of electrocatalysts

3.1.1 Boron-doped carbon and their references

1) Boron-doped carbons (BDC700 and BDC900)

High-grade tetraphenylboron sodium (99.5%, ACROS) was used as a single precursor. Solid-state pyrolysis was conducted using commercial Swagelok union cells. 0.4 g of the precursor was filled into the cell at room temperature under atmospheric condition. The tightly closed cell was then placed in the center of a tubular furnace. The temperature was raised at a heating rate of 15 °C min⁻¹ up to the required temperature (700 °C and 900 °C), and the temperature was maintained for 3 h. After complete solid-state pyrolysis of the precursor, the cell was gradually cooled to room temperature. The entire process was conducted under autogenic conditions with no gas flow. The products prepared at 700 °C and 900 °C were denoted as BDC700 and BDC900, respectively. As-prepared BDCs were treated with 10 mL of concentrated HCl (~37.0%) for 24 h to dissolve any oxide on the surface of the as-prepared BDCs. Next, acid treated BDCs were stirred with 50 mL of distilled water at 80 °C for 30 min to remove any borate derived from non-doped boron into the carbon network. Lastly, the BDCs were washed by using copious ethanol, and the washed BDCs were dried overnight in a vacuum oven at 60 °C.

All supernatants such as used HCl, distilled water, and ethanol were removed by using centrifugal separation at a rotation speed of 10000 rpm for 10 min.
2) Non-boron-doped carbons (Cs)

Tetraphenylmethane (96%, Alfa Aesar) was used as a single precursor to prepare catalysts. 0.2 g of the precursor was filled into a Swagelok union cell. The tightly closed cell containing the precursor was thermally then decomposed under the same conditions as pyrolysis of BDCs. The products prepared at 700 °C and 900 °C were named as C700 and C900, respectively.

For purification of as-prepared Cs, HCl treatment was performed to remove oxide species. Acid treated Cs were washed by using copious distilled water and ethanol, and then all supernatants were extracted by centrifugal separation. Washed Cs were dried at 60 °C under a vacuum atmosphere.

3.1.2 Phosphorus or boron-selective-doped graphene and their references

1) Phosphorus or boron-selective-doped graphene (PDG700 and BDG900)

Targeting products, PDG700 and BDG900, were fabricated by solid-state pyrolysis of a readily available mixture of commercial graphene (N002-PDR, Angstrom materials) as carbon source and tetraphenylphosphonium tetraphenylborate (TPP TPB, Aldrich) as a single precursor for B and P. For well-combined mixture, graphene dispersion and TPP TPB solution were prepared with sonication for 30 min. The graphene dispersion consists of 100 mg of graphene and 10 mL of ethanol; the TPP TPB solution consists of 200 mg of TPP TPB and 10 mL of ethanol. The TPP TPB solution was added slowly into the graphene solution with magnetic stirring and heating at a temperature of 60 °C. Once the addition of TPP TPB solution was finished, the temperature was kept for 6 h with continuous stirring. After 6 h, ethanol was removed by centrifugal separation, and dried at 60 °C under vacuum. Afterwards, B and P impregnated graphene was obtained in the form of black powder, which is named as BPG precursor. 0.035 g of the BPG precursor was enclosed in a Swagelok cell; subsequently it was thermally decomposed at a temperature of 700 °C and 900 °C for 3 h in a tubular furnace under...
autogenic atmosphere. The cell was cooled under ambient conditions. The BPG precursor calcined at 700 °C and 900 °C was named as PDG700 and BDG900, respectively. Naming of PDG and BDG is derived from a kind of heteroatom. The kind of heteroatom that is doped into the graphene was determined by elemental composition analysis using X-ray photoelectron spectroscopy (XPS). PDG corresponds to phosphorus-doped graphene, and BDG is equal to boron-doped graphene.

As-prepared PDG700 and BDG900 were treated with 10 mL of concentrated HCl (~37.0%) for 24 h to dissolve any oxide on the surface of the as-prepared PDG700 and BDG900. Acid treated samples were washed by using copious distilled water and ethanol, and dried overnight in a vacuum oven at 60 °C.

All supernatant such as used HCl, distilled water, and ethanol were removed by using centrifugal separation at a rotation speed of 10,000 rpm for 10 min.

2) Pristine graphene

For comparison, untreated pristine graphene was used as reference catalyst, which is the same product as used when the target catalysts were fabricated.
Figure 3-1. Chemical structure of precursors: (a) tetraphenylboron sodium for BDCs, (b) tetraphenylmethane for Cs, and (c) tetraphenylphosphonium tetraphenylborate for PDG700 and BDG900.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Chemical formula</th>
<th>Atomic distribution (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraphenylboron sodium</td>
<td>C_{24}H_{20}BNa</td>
<td>52.2 43.4 2.2 - 2.2</td>
</tr>
<tr>
<td>Tetraphenylmethane</td>
<td>C_{25}H_{20}</td>
<td>55.6 44.4 - - -</td>
</tr>
<tr>
<td>Tetraphenylphosphonium tetraphenylborate</td>
<td>C_{48}P_{48}BP</td>
<td>53.3 44.5 1.1 1.1 -</td>
</tr>
</tbody>
</table>

Table 3-1. Atomic distribution (at.%) of precursors depicted in Figure 3-1
3.2 Characterization

3.2.1 Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) studies were conducted to investigate the thermal behavior of the precursor by using TGA (TA instrument, Q600), and to predict the pyrolysis yield of the precursor. The experiment was performed in an alumina pan under a closed system (no gas flow). The temperature was raised at 15 °C min\(^{-1}\) from 25 °C to 1000 °C.

3.2.2 Electron microscope study

Electron microscope studies were conducted to confirm the morphology and \(d\)-spacing (interlayer distance) by using FE-SEM (Hitachi, S-4800 II) and FE-TEM (Hitachi, HF-3300). Samples for the microscope experiments were prepared by dropping ultrasonically dispersed solution of BDCs and isopropyl alcohol on a substrate. As the substrate, commercial aluminum foil (5 mm \(\times\) 5 mm) was used for SEM while a copper grid coated with amorphous carbon film was used for TEM measurements. TEM experiments were performed at an acceleration voltage of 300 kV. For the elemental mapping study, an EDS (energy dispersive x-ray spectroscopy) connected to a TEM was used for each samples in scanning TEM mode.

3.2.3 X-ray diffraction (XRD) study

The nature of crystallinity of products was studied by powder XRD (Panalytical, Empyrean) using Cu K-alpha radiation at a generator voltage of 40 kV and a tube current of 30 mA.
3.2.4 Raman spectroscopic study

To inspect the nature of carbon with a ratio of structural defects to graphitic array, Raman spectroscopy was obtained by high resolution dispersive Raman microscope (Horiba Jobin Yvon, LabRAM HR UV/Vis/NIR).

3.2.5 X-ray photoelectron spectroscopic (XPS) study

Elemental analysis was performed by XPS (Thermo Fisher Scientific, ESCALAB250 XPS system, Theta Probe XPS system) using monochromated Al K-alpha source at 15 kV and 150 W. Binding energy values at the x-axis were calibrated by using C 1s from a carbon value taken as 284.6 eV.

3.2.6 Electrochemical study

To study the electrocatalytic performance of BDCs, PDG700, and BDG900 for the ORR, electrochemical analysis using potentiostat (Bio-Logic, VSP) was studied by using cyclic voltammetry (CVs) and linear sweep voltammetry (LSVs) with a 3-electrode system. For the 3-electrode system, a saturated calomel electrode (SCE, Hg/HgCl), a spiral platinum wire, and a glassy carbon electrode (GCE, Ø = 3 mm) were used as a reference, counter, and working electrode, respectively. The voltammograms were recorded in N₂-saturated 0.1 M KOH aqueous solution at a scan rate of 10 mVs⁻¹. The N₂ and O₂-saturated electrolytes were prepared by bubbling nitrogen and oxygen gas for 30 min at a flow rate of 80 sccm, respectively. For the working electrode, bare glassy carbon stuck in Teflon was used. On the bare glassy carbon electrode (GCE), catalyst ink was dropped on the surface, and dried at 50 °C in a forced convection oven; afterwards, Nafion® 5 wt% solution (Aldrich) was dropped on the top of dried catalyst ink. Nafion® was used as binder to hold
the catalyst to the GCE. The preparation method of catalyst ink, and loading amount of catalyst ink and binder was optimized depending on each catalyst and technique.

All experiments were continued until the stable voltammogram was obtained. Potential values were converted from vs. SCE to vs. Reversible Hydrogen Electrode (RHE), and current was normalized to the geometric area of electrode. To convert current to current density, current values were divided into geometric area of glassy carbon electrode (0.0707 cm$^2$). For comparison, 10 wt% loaded Platinum on carbon black, Vulcan XC-72, (E-TEK) was used as a reference catalyst.

1) Catalyst ink preparation

(1) Boron-doped carbon (BDC700 and BDC900)

The catalyst ink was prepared using a mixture of 5 mg of black powdered BDCs and 100 µL of isopropyl alcohol (IPA) in 1.5 mL. The mixture was sonicated for 30 min using a sonicator.

(2) Phosphorus or boron-selective-doped graphene (PDG700 and BDG900)

The catalyst ink was prepared with 1 mg of black powdered PDG700 and BDG900, and 100 µL of aqueous solution (distilled water: 75 µL, Nafion$^{\circledR}$ 5 wt% solution: 20 µL, IPA: 5 µL). The ink was vigorously sonicated for 30 min using a sonicator.
2) Cyclic voltammetric (CV) technique

The working electrode was prepared by dropping 10 µL of catalyst ink on the surface of the electrode at first, and then 5 µL of Nafion® 5 wt% solution (Aldrich) was dropped on the same area. Afterwards, a GCE was dried. The same catalyst ink was used for LSV experiments. Catalyst ink covered the whole area of the bare working electrode. The static electrode technique was used.

3) Linear sweep voltammetric (LSV) technique

For BDCs, 30 µL of catalyst ink and 10 µL of Nafion® 5 wt% solution (Aldrich) were dropped on the surface of the GCE, and catalyst ink covered the whole area of the bare working electrode. For PDG700 and BDG900, 5 µL of catalyst ink was dropped firstly, and then 2 µL of Nafion® 5 wt% solution (Aldrich) was dropped on the GCE. The catalyst ink covered only the glassy carbon. The rotating disk electrode (RDE) technique was used at an electrode rotating speed from 400 rpm to 2500 rpm (400, 800, 1200, 1600, 2000, and 2500 rpm). O₂ bubbling was kept at a flow rate of 20 sccm during the LSV experiments.

3.2.7 Selectivity study: methanol oxidation tolerance and CO poisoning test

A methanol oxidation tolerance test was conducted to investigate the methanol crossover effect of catalysts when the catalysts are applied to a direct methanol fuel cell (DMFC). DMFC has suffered from mixed potential of methanol oxidation and oxygen reduction at cathode due to methanol crossover through membrane (electrolyte) from anode to cathode. Thus, use of the catalyst possessing methanol oxidation tolerance can minimize the effect of methanol crossover.

CO poisoning effect is also a performance degrading factor for fuel cells. CO gases generated by oxidation of carbon support were adsorbed on the surface of fuel cell catalysts, and then
the active surface area of catalysts is dramatically decreased. This decrease leads overall performance degradation of the fuel cell. Therefore, an ability to tolerate the CO poisoning effect is important in fuel cell catalysts.

1) Boron-doped carbon (BDC700 and BDC900)

For BDCs, chronopotentiometric (CA) technique was used with RDE technique and a 3-electrode system for both methanol oxidation tolerance and CO poisoning effect tests. The 3-electrode system was used with the same reference, counter, and working electrode as the electrochemical study.

A methanol oxidation tolerance test was performed at a potential of -0.5 V vs. SCE for 2500 s at an electrode rotation speed of 1600 rpm. 2 mL of 2 M methanol aqueous solution was added in O₂-saturated 0.1 M KOH aqueous solution at 650 s. Response owing to methanol addition appeared 10 min after addition of methanol (1250 s) since a perfect mix of electrolyte and added methanol requires around 10 min (600 s).

Catalyst poisoning effect was investigated under CO existence at a potential of -0.5 V vs. SCE for 2500 s at a scan rate of 1600 rpm. To consider decreased partial pressure effect of O₂ gas in electrolyte due to the addition of CO gas, additional experiments were performed with the addition of N₂ gas instead of CO gas. CO and N₂ bubbling began at 1250 s at a flow rate of 20 sccm, which is the same as that of O₂ bubbling. For the experiment, mixed gas with 10% CO and 90% N₂ was used as a CO source.

During the experiments, O₂ bubbling was continuously maintained with a flow rate of 20 sccm for O₂ saturation environment.
2) Phosphorus or boron-selective-doped graphene (PDG700 and BDG900)

For PDG700 and BDG900, linear sweep voltammetric (LSV) technique was used with RDE technique and 3-electrode system for both methanol oxidation tolerance and CO poisoning effect tests. The 3-electrode system was used with the same reference, counter, and working electrode as the electrochemical study.

Methanol oxidation tolerance and CO poisoning effect tests were conducted at a potential window of 0.2 V to -0.8 V at a scan rate of 10 mVs⁻¹ at an electrode rotation speed of 1600 rpm. O₂-saturated 0.1 M KOH was used as electrolyte. The experiments were conducted under two different environments. The first LSV was obtained in O₂-saturated electrolyte. Afterwards, the second LSV was obtained in 2 mL of 2 M methanol added O₂-saturated electrolyte. To consider enough mix of methanol in electrolyte, the experiment started 10 min after the addition of methanol. O₂ bubbling was kept at a flow rate of 20 sccm during the experiments.

CO poisoning effect test was investigated under three different environments. The first LSV was obtained in O₂-saturated 0.1 M KOH electrolyte. The second LSV was obtained in both CO and O₂-saturated electrolyte. To consider decreased partial pressure effect of O₂ gas in electrolyte due to addition of CO gas, the third LSV was obtained in both N₂- and O₂-saturated electrolyte. During the experiments, all gases bubbling, O₂, CO, N₂, were kept at a flow rate of 20 sccm.

Other unmentioned experimental parameters were set the same as the BDCs experiments.

3.2.8 Durability test

A durability test under continuous oxygen reduction was conducted by using the chronoamperometric response using the RDE technique at a fixed potential of -0.26 V vs. SCE for 43200 s (12 h) with an electrode rotation speed of 1600 rpm. The fixed potential was set within the kinetic region. A 3-electrode system was used with the same reference, counter, and working electrode as the previous
electrochemical study. For electrolyte, O\textsubscript{2}-saturated 0.1 M KOH aqueous solution was prepared by O\textsubscript{2}-bubbling at a flow rate of 80 sccm for 30 min. During the experiments, O\textsubscript{2} gas bubbling was maintained at 20 sccm. The data was recorded every 100 µA and 5 s.

To quantify methanol tolerance durability, normalized current was calculated for each sample. Afterwards, the normalized current was converted to percentage using the following equation:

\[
\text{Relative current} \%(\%) = \frac{\text{Normalized current}}{\text{Normalized current}} \times 100 \%(\%) = \frac{J}{J_0} \times 100 \%(\%) \quad (3.1)
\]
IV. Results and discussion

4.1 Boron-doped carbon

4.1.1 Thermo-gravimetric analysis (TGA)

In Figure 4-1 (a), pyrolysis yield of tetraphenylboron sodium is found to be 54.84% and 53.37% at 700 °C and 900 °C, respectively. These values are slightly higher than the actual pyrolysis yield of 51.14% and 51.29% at 700 °C and 900 °C, respectively. After purification of the as-synthesized samples, the pyrolysis yields were obtained 37.04% for BDC700 and 31.61% for BDC900. The decrease in the yield from 51.14% to 37.04% and from 51.29% to 31.61% is attributed to the removal of impurities including metal oxide and sodium borate. The metal oxide is derived from the metallic Swage union cell, and the sodium borate is due to the precursor.

The yield of C700 and C900 are found to be 38.45% and 45.89%. The obtained yields are slightly higher than the expected yield based on the thermo-gravimetric analysis of the precursor (21.58% and 21.13%). The yield declined to 13.87% and 16.94% for C700 and C900 after purification. The decreased yield is owing to the removal of heavy metal oxides such as iron oxide and chromium oxide.
Figure 4-1. Thermograms of (a) tetraphenylboron sodium (precursor for BDCs) and (b) tetraphenylmethane (precursor for Cs).
4.1.2 Electron microscope study

1) Morphology study by using SEM and TEM

The morphology analysis by SEM reveals that BDC700 and BDC900 show the presence of rod-like structures and are stacked together (Figure 4-2 (a) and (c)). The rods have a uniform width and length of about 1-5 μm and 4-17 μm, respectively. The cross sectional study of the rod exhibits the presence of tiny convex caps on the surface of the cross section area (Figure 4-2 (b) and (d)).

In the TEM image, an individual rod (sheet) is shown in Figure 4-2 (e). The high resolution TEM image shows that the interlayer distance between the two planes of BDC900 is about 0.36 nm (Figure 4-2 (f)), which corresponds to the (002) crystal plane of graphite (0.335 nm). Although the \( d \)-spacing of BDC900 is wider than that of the (002) crystal plane of graphite, it is difficult to consider that boron doping results in \( d \)-spacing expansion because the starting material for fabricating BDC900 is not graphite or graphene.

2) Elemental mapping study by using scanning TEM

The elemental mapping study by using scanning TEM indicates that the presence of carbon, boron, and oxygen in BDC900 as shown in Figure 4-3. For investigation of elemental composition in the samples, XPS analysis was conducted, and the results will be discussed in subsequent sections.
Figure 4-2. (a) Low resolution and (b) high resolution SEM image of BDC700, (c) low resolution and (d) high resolution SEM image of BDC900, (e) low resolution and (f) high resolution TEM image of BDC900.
Figure 4-3. (a) Bright field image of BDC900 and elemental mapping of (b) carbon, (c) boron, (d) oxygen, (e) overlap of C, B, and O, and (f) overlap of C and B.
4.1.3 X-ray diffraction (XRD) study

The powder XRD pattern of BDCs without any impurity peaks indicates all impurities were removed during the purification steps.

The XRD pattern of BDC900 shows a broad diffraction peak at 24.3 °, which corresponds to graphitic carbon (002) diffraction, with an interlayer distance of around 0.367 nm (Figure 4-4). The interlayer distance value obtained in XRD is closely matched with the value observed in HR-TEM results, ~0.36 nm. The d-spacing value observed for BDCs is consistent with the reported values. For instance, Sheng et al.\textsuperscript{13} observed a interlayer distance of ~0.37 nm from a TEM image and ~0.35 nm from PXRD for boron-doped graphene.

On the other hand, the interlayer distance of BDC700 was measured at 0.402 nm at 22.1 °, which is slightly higher than that of BDC900. This difference may be due to difference of boron compositions that are 3.1 at.% and 4.05 at.% from wide XPS spectra for BDC700 and BDG900, respectively. In other words, the interlayer distance is contracted in the sample that has more boron. For this reason, Hagio et al.\textsuperscript{28} suggested that the contraction of the interlayer distance may be attributed to a decrease in repulsion between graphite layers. The decrease in repulsion is owing to a decrease of π electron density after boron doping because the boron atom has one fewer valence electron than the carbon atom.

Higher pyrolysis temperature of BDC900 can be a one evidence for smaller distance of BDC900 than BDC700. Takai et al.\textsuperscript{58} and Endo et al.\textsuperscript{69} reported that high temperature treatment decreases in interlayer spacing.
4.1.4 Raman spectroscopic study

The Raman spectra of BDCs exhibit the presence of two strong peaks at 1367 cm\(^{-1}\), 1588 cm\(^{-1}\) for BDC700 and 1364 cm\(^{-1}\), 1567 cm\(^{-1}\) for BDC900. The bands observed at 1367 cm\(^{-1}\), 1364 cm\(^{-1}\) and 1588 cm\(^{-1}\), 1567 cm\(^{-1}\) correspond to D and G bands of carbon, respectively. (Figure 4-5). Commonly, it is known that the D and G band is derived from the existence of sp\(^3\) defect sites and sp\(^2\)-boned pairs, respectively. The sp\(^3\) defected carbon is due to distortion; the sp\(^2\) carbon is due to graphitic carbon array. Accordingly, the ratio between intensities of D band and G band, \(I_D/I_G\), is an effective tool to ascertain the quality and the nature of carbon. The near zero value of \(I_D/I_G\) means high crystallinity, and a value near one indicates a high portion of structural defects in carbon framework.\(^{70}\) The \(I_D/I_G\) for both BDC700 and BDC900 is around 0.95 (BDC700: 0.947, BDC900: 0.953), which is insignificant difference between the two samples. This result suggests that BDCs have more disordered carbon (defects) than ordered graphitic carbon. Hagio et al.\(^{28}\) reported that boron doping contributes structural defects to around substitutional boron atoms in the parent graphite lattice. Some researchers\(^{12,13,42,71}\) also reported an increasing \(I_D/I_G\) ratio due to boron doping into the carbon network regardless of the types of carbon, which are crystal or amorphous.

The existence of more defects in BDCs is attributed to the doped boron into the hexagonal sites of the carbon network. The defect sites in BDCs can contribute to provide more reaction sites for the oxygen adsorption and subsequent reduction.
**Figure 4-4.** XRD patterns of BDCs.

**Figure 4-5.** Raman spectra of BDCs.

**4.1.5 X-ray photoelectron spectroscopic (XPS) study**
The XPS survey spectra exhibit the presence of C, O, Na, and B (Figure 4-6) in both BDC700 and BDC900. The composition of C, O, Na, and B is given in the Table 4-1. Boron 1s peak is observed at a binding energy of 191 eV in both BDCs (BDC700; 191.27 eV, BDC900; 191.36 eV), which is positively shifted compared to the binding energy of pure B1s peak (187 eV). The shift of B1s peak is attributed to the formation of B-C bonding.\textsuperscript{13,15} From XPS quantitative analysis, the ratio of doped B into C (B/C) for BDC700 and BDC900 is found to be 3.8% and 5.3%, respectively. The B/C ratio of BDC900 is 1.4 times higher than that of BDC700. After deconvolution of high resolution B1s spectrum, the B1s spectra on both BDC700 and BDC900 are separated into four components, as shown in Figure 4-7. For BDC700, the highest binding energy, 192.6 eV, is assigned to BCO\textsubscript{2}. The peak at 191.1 eV is due to BC\textsubscript{2}O. The peaks centered at 189.5 eV and 187.3 eV correspond to BC\textsubscript{3} and B\textsubscript{4}C, respectively. For BDC900, the peak at 192.9 eV is assigned to BCO\textsubscript{2}, and the peak at 191.4 eV is derived from BC\textsubscript{2}O. The peaks due to BC\textsubscript{3} and B\textsubscript{4}C are obtained at binding energy centered at 189.4 eV and 186.9 eV, respectively. The binding energy values for the four components are close to reported value in literatures. For example, Yang et al.\textsuperscript{12} reported that the peaks of BCO\textsubscript{2}, BC\textsubscript{2}O, BC\textsubscript{3}, and B\textsubscript{4}C were detected at a binding energy of 192.3 eV, 191.0 eV, 189.5 eV and 187.5 eV in boron-doped carbon nanotube (B\textsubscript{3}CNT), respectively. Sheng et al.\textsuperscript{13} observed that the peaks of BCO\textsubscript{2}, BC\textsubscript{2}O, BC\textsubscript{3}, and B\textsubscript{4}C were found at a binding energy of 191.9 eV, 190.4 eV, 189.0 eV and 187.7 eV, respectively. Analysis of the B1s spectra reveals higher total composition of B-C bonding (BC\textsubscript{3} and B\textsubscript{4}C) in BDC900 (42.2%) than that of BDC700 (37.7%), indicating that the carbon framework of BDC900 is electronically modified more than that of BDC700. In particular, B\textsubscript{4}C and BC\textsubscript{3} species were dominant in BDC700 and BDC900, respectively (Table 4-1). Furthermore, different dominant species in BDC700 and BDC900 can be evidence to investigate difference of ORR performance between two catalysts.
**Figure 4-6.** Wide XPS spectra of BDC700 and BDC900.

**Table 4-1.** Composition of C, O, Na, and B in BDC700 and BDC900 based on Figure 4-6 and 4-7

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic percent (at.%)</th>
<th>Boron distribution (at.%)</th>
<th>B/C ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
<td>Na</td>
</tr>
<tr>
<td>BDC700</td>
<td>81.03</td>
<td>15.30</td>
<td>0.57</td>
</tr>
<tr>
<td>BDC900</td>
<td>76.74</td>
<td>16.12</td>
<td>3.09</td>
</tr>
</tbody>
</table>
Figure 4-7. High resolution XPS spectra of B1s of (a) BDC700 and (b) BDC900.
4.1.6 Electrochemical study

1) Cyclic voltammetric studies

The cyclic voltammograms (CVs) of C700 and C900, which is non-doped carbon, exhibit broad cathodic peaks at 0.57 V and 0.50 V vs. RHE (Figure 4-8 (a) and (b)) with a peak current of -0.18 mAcm$^{-2}$ and -0.44 mAcm$^{-2}$. However, BDCs show an oxygen reduction current with a well-defined cathodic peak at 0.67 V and 0.66 V vs. RHE for BDC700 and BDC900, respectively (Figure 4-8 (c) and (d)). It demonstrates that boron doping improves the ORR activity of BDCs. Furthermore, the peak current of BDC700 and BDC900, -1.21 mAcm$^{-2}$ and -2.37 mAcm$^{-2}$, is significantly higher than that of C700 and C900. The current density difference between background and oxygen reduction curve at a point of 0.65 V vs. RHE shows also big difference between Cs and BDCs. The potential of 0.65 V vs. RHE is one point within kinetically active region. This improved current in BDC is ascribed to an increase in conductivity due to lowered Fermi energy level of carbon-based materials due to boron doping, as reported by Burgess et al.$^{71}$ and Mele et al.$^{72}$

The onset potential is another critical factor to investigate the ORR kinetics with the peak current. The more positive onset potential indicates faster kinetics of the ORR.$^{3,34}$ Onset electrode potential was defined in two ways by Takasu et al.$^{73}$ The first is the potential where the cathodic current begins to be observed on the voltammogram, and the second is the potential where the additional cathodic current attained 20 μA/cm$^2$-(geometric). Between the two methods, the later method was adopted in this work. The onset potential values of the ORR shift more positively after boron doping, which is from 720 mV to 740 mV between C700 and BDC700; from 730 mV to 770 mV between C900 and BDC900. The more positive onset potential corresponds to less overpotential in fuel cells, which results in enhanced catalytic activity. The enhancement of catalytic activity for the ORR in BDCs is attributed to the charge localization to neighboring carbon atoms around substitutional boron, which is due to boron doping into the carbon network charge delocalized.$^{18,26}$ In fact, atomic charge delocalization on heteroatom-doped carbon can be sites where oxygen is adsorbed.
O$_2$ adsorption is one important step for subsequent oxygen reduction.$^{9,13,46}$ In addition, asymmetric spin density introduced by heteroatom doping can be a factor to improve ORR catalytic activity.$^{46}$

2) Rotating disk electrode (RDE) technique

To further understand the kinetics of oxygen reduction activity of the BDCs, hydrodynamic LSVs was performed at various rotation speeds from 400 rpm to 2500 rpm. In LSVs of BDC700 and BDC900, current density is increased as the electrode rotation speed increases (Figure 4-9 (a) and (b)). The corresponding Koutecky-Levich plot (Figure 4-9 (c) and (d)) of BDCs exhibits good linearity and parallelism that indicate the ORR on the catalyst follows a first-order kinetics over a wide potential range.$^{40}$ The slope of the K-L plots is constant, which infers that the electron transfer number of the ORR is similar at different potential.$^{40}$

ORR activity was improved when increasing the pyrolysis temperature from 700 °C to 900 °C. BDC900 shows higher ORR performance than BDC700. To compare ORR activity among BDC700, BDC900, and commercial Pt/C catalyst, linear sweep voltammogram using RDE traces were obtained at a scan rate of 10 mVs$^{-1}$ with 1600 rpm. The results of this comparison are shown in Figure 4-10. The kinetic parameter was calculated by the Koutecky-Levich equation (Eq. 2.4) and organized in Table 4-3. Calculated $n$ value of BDC700 and BDC900 was 1.88 and 3.73 at 0.45 V vs RHE at 1600 rpm. The electron transfer number of BDC900 suggests that BDC900 leads the ORR to follow single step reaction by a four-electron pathway, which is comparable with that of Pt/C, 3.98. The kinetic current density ($J_k$) at 0.65V vs. RHE was obtained by extrapolation of y-intercept of the K-L plot. The $J_k$ of BDC700, BDC900, and Pt/C is 0.75 mAcm$^{-2}$, 3.53 mAcm$^{-2}$ and 32.9 mAcm$^{-2}$, respectively. BDC900 exhibits higher kinetic current density than the BDC700; however, the value of the BDC900 is much lower than that of Pt/C. The onset potential of BDC700, BDC900, and Pt/C is 0.71 V, 0.76 V, and 0.98 V vs. RHE in 0.1 M KOH electrolyte. Although the onset potentials of BDCs are 0.2 V less than that of Pt/C, the values are similar to other boron-doped carbon based materials that is in the range of 0.695 V ~ 0.73 V vs. RHE.$^{9,12,13,20}$ Although the electron transfer number and
kinetic order are comparable with commercial Pt-based catalysts, the enhancement of onset potential for faster kinetics still remains as challenges in field of non-precious metal-free catalysts.

In comparing ORR activities between BDC700 and BDC900, the BDC900 exhibited higher ORR performance than BDC700. The difference of electrocatalytic activity for the ORR between BDC700 and BDC900 is attributed to the composition and quality of boron doped into the carbon network. BDC900 exhibits a higher content of active sites (BC$_3$ and B$_4$C) present in the carbon network than the BDC700. This is corroborated by a quantitative XPS analysis of BDC900. The results from the XPS analysis exhibited higher total doped boron (BC$_3$ and B$_4$C) in the carbon network than BDC700. Importantly, between the two components, the presence of BC$_3$ composition (BDC700:12.7%, BDC900:22.4%) in the catalysts is considered as the main evidence to cause enhancement of the ORR activity in BDC900.
Figure 4-8. Cyclic voltammograms of (a) C700, (b) C900, (c) BDC700, and (d) BDC900. Dotted line for N₂-saturated 0.1 M KOH and solid line for O₂-saturated 0.1 M KOH.

Table 4-2. Comparison of the ORR activity of Cs and BDCs by CV technique

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset potential (V vs. RHE)</th>
<th>Peak current (mACm²)</th>
<th>Current density difference at 0.65 V vs. RHE (mACm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C700</td>
<td>0.72</td>
<td>-0.18</td>
<td>0.03</td>
</tr>
<tr>
<td>BDC700</td>
<td>0.74</td>
<td>-1.21</td>
<td>0.65</td>
</tr>
<tr>
<td>C900</td>
<td>0.73</td>
<td>-0.44</td>
<td>0.21</td>
</tr>
<tr>
<td>BDC900</td>
<td>0.77</td>
<td>-2.38</td>
<td>1.71</td>
</tr>
</tbody>
</table>
Figure 4-9. Hydrodynamic linear sweep voltammograms (LSVs) of the ORR on (a) BDC700 and (b) BDC900 in 0.1 M KOH at 10 mVs$^{-1}$ at various electrode rotation speeds. Corresponding K-L plots of (c) BDC700 and (d) BDC900.
Figure 4-10. LSVs of the ORR on BDC700, BDC900, and Pt/C in 0.1 M KOH at a scan rate of 10 mVs$^{-1}$ at 1600 rpm.

Table 4-3. Electrocatalytic parameter for the ORR of BDC700, BDC900, and Pt/C by hydrodynamic linear sweep voltammetry

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset potential (V vs. RHE)</th>
<th>Electron transfer (n) at 0.45 V vs. RHE</th>
<th>Kinetic current density ($J_k$) at 0.65 V vs. RHE (mAcm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDC700</td>
<td>0.71</td>
<td>1.88</td>
<td>0.75</td>
</tr>
<tr>
<td>BDC900</td>
<td>0.76</td>
<td>3.73</td>
<td>3.53</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.98</td>
<td>3.98</td>
<td>32.9</td>
</tr>
</tbody>
</table>
4.1.7 Selectivity and durability study

1) Selectivity study: methanol oxidation tolerance and CO poisoning test

A selectivity test for ORR was performed by evaluating methanol tolerance (Figure 4-11 (a)). Commercial Pt/C catalyst displays a dramatic decay of relative current at an instant 10 min after 2 mL of 2 M methanol aqueous solution was added in O₂-saturated electrolyte. To completely mix the added methanol in electrolyte, around 10 min was required. On the other hand, the relative current of BDC700 and BDC900 is maintained after the addition of methanol. This finding indicates that BDCs have both the selectivity for ORR and the capability to avoid mixed potential under methanol crossover.

CO poisoning effect was investigated (Figure 4-11 (b)), and quantified by comparison of decay of current between two experiments that are N₂ addition and CO addition experiments. In BDC900, current decay due to the addition of CO (53.6%) is similar to that of the addition of N₂ (50.2%). This similarity suggests that the current decay in CO addition experiments is due to a decrease in O₂ solubility in electrolyte partial pressure resulted from decline in O₂ partial pressure. Otherwise, in Pt/C, current after the addition of CO decreases to 32.5%, which is around two times less than the current decay after the addition of N₂ (64.7%). This result suggests that BDC900 has greater CO tolerance than commercial Pt/C catalyst.

2) Durability test

A durability test was performed for 12 h (43200 s). The decrease in the relative current of the commercial Pt/C is found to be 63.4%. However, BDC900 shows excellent durability in comparison with Pt/C. The decrease in the relative current of BDC900 is found to be 83.1% (Figure 4-12). This finding suggests that BDC900 has outstanding long-term stability in ORR in alkaline medium.
Figure 4-11. Chronoamperometric response of BDC900 and Pt/C at -0.5 V vs. SCE in O$_2$-saturated 0.1 M KOH solution (a) with addition of 2 M methanol at 650 s and (b) with addition of CO (red line) and N$_2$ gases (black line) at 1250 s at the same flow rate as O$_2$ gas.
Figure 4.12. Chronoamperometric response of BDC900 and Pt/C at -0.26 V vs. SCE in O₂-saturated 0.1 M KOH solution for durability test during 12 h (43200 s).
4.2 Phosphorus or boron-selective-doped graphene

4.2.1 Thermo-gravimetric analysis (TGA)

Actual pyrolysis yields of PDG700 and BDG900 from a BPG precursor were found to be 45.80% and 47.86%, respectively. The BPG precursor was prepared by mixing tetraphenylphosphonium tetraphenylborate and graphene powder. After purification of the as-synthesized samples, the yield was decreased from 45.80% to 44.17% in PDG700 and from 47.86% to 34.09% in BDG900. These decreases are due to the removal of heavy metal oxide during the purification step. Although heavy impurities are removed, the actual yields are slightly higher than the expected yield based on the thermo-gravimetric analysis of the precursor, as shown in Figure 4-13. The higher yields than the expected values are attributed to higher pressure that is put to the precursor at high temperature in a Swagelok union cell. Although a closed cell is used for TGA, the Swagelok union cell provides higher pressure because the Swagelok cell is tightly closed by using two terminal screws. The higher pressure cause slower decomposition of the precursor, as reported by Fatemi et al.\textsuperscript{75} and Whitty el al.\textsuperscript{76}
Figure 4-13. Thermogram of BPG precursor prepared by using tetraphenylphosphonium tetraphenylborate and graphene.
4.2.2 Electron microscope study

1) Morphology study using SEM and TEM

Morphological studies using TEM reveal the graphene-like structure of PDG700 and BDG900 (Figure 4-14). In a low resolution TEM image, thin sheet-like structures with random wrinkles were observed in both PDG700 and BDG900, which is the same morphology as pristine graphene. A high resolution TEM image suggests that the interlayer distance values of PDG700, BDG900, and commercial pristine graphene were 0.341 nm, 0.338 nm, and 0.339 nm, respectively. The evidence for the difference of the interlayer between prepared samples and pristine graphene will be discussed with XRD data.

2) Elemental mapping study by using scanning TEM

An elemental mapping study using scanning TEM shows the presence of carbon and phosphorus in the PDG700 and the presence of carbon and boron in the BDG900, as shown in Figure 4-15 and 4-16. For investigation of elemental composition in the samples, XPS analysis was conducted, and the results will be discussed in subsequent sections.
Figure 4-14. Low resolution TEM image of (a) PDG700, (c) BDG900, and (e) pristine graphene. High resolution TEM image of (b) PDG700, (d) BDG900, and (f) pristine graphene with fringes.
Figure 4-15. (a) Bright field image of PDG700 and elemental mapping of (b) carbon, (c) boron, and (d) overlap of C and B.

Figure 4-16. (a) Bright field image of BDG900 and elemental mapping of (b) carbon, (c) phosphorus, and (d) overlap of C and P.
4.2.3 X-ray diffraction (XRD) study

The XRD pattern of PDG700 and BDG900 without any impurity peaks exhibits a broad diffraction peak at 24.4 ° and 25.2 ° with interlayer distances of 0.366 nm and 0.353 nm. The numeric order of interlayer distances obtained from XRD results, which show BDG900 having smaller values than PDG700, is matched with those measured by TEM.

A comparison of prepared samples and pristine graphene found that an interlayer distance of PDG700 and BDG900 is narrower than that of untreated graphene. This tendency results from the higher effect of high temperature treatment, at 700 °C and 900 °C, than heteroatom doping effect. Takai et al.68 and Endo et al.69 reported that high temperature treatment decreases in interlayer spacing.

In comparison with the interlayer distance of PDG700 and BDG900, the value of BDG900 is smaller than that of PDG700. This difference is ascribed to the similar covalent radius of the boron atom embedded in BDG900 to the parent carbon atom, while around 1.5 times bigger covalent radius of the phosphorus atom embedded in PDG700 than that of the carbon atom. The covalent radius of carbon, boron and phosphorus is 77 pm, 88 pm, and 110 pm, respectively.45 Higher pyrolysis temperature of BDG900, which is 200 °C higher than that of PDG700, can be another factor to influence the wider interlayer distance of BDG900 over PDG700.
**Figure 4-17.** XRD patterns of PDG700, BDG900, and pristine graphene.

**Table 4-4.** Interlayer distance of PDG700, BDG900, and pristine graphene measured by using XRD and TEM

<table>
<thead>
<tr>
<th>Sample</th>
<th>Interlayer distance (nm)</th>
<th>XRD results</th>
<th>TEM results</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDG700</td>
<td>0.366 (at 24.3 °)</td>
<td></td>
<td>0.341</td>
</tr>
<tr>
<td>BDG900</td>
<td>0.353 (at 25.2 °)</td>
<td></td>
<td>0.338</td>
</tr>
<tr>
<td>Pristine graphene</td>
<td>0.369 (at 24.1 °)</td>
<td></td>
<td>0.339</td>
</tr>
</tbody>
</table>
4.2.4 Raman spectroscopic study

The Raman spectra in Figure 4-18 show the presence of two strong peaks at 1341 cm\(^{-1}\), 1584 cm\(^{-1}\) for PDG700 and 1343 cm\(^{-1}\), 1578 cm\(^{-1}\) for BDG900. The bands observed at 1341 cm\(^{-1}\), 1343 cm\(^{-1}\) and 1584 cm\(^{-1}\), 1578 cm\(^{-1}\) correspond to D and G bands of carbon, respectively. The \(I_D/I_G\) ratio for PDG700 and BDG900 is 1.03 and 1.36, respectively. In common, two prepared samples have more sp\(^3\) disordered carbon, related to D band, than sp\(^2\) ordered carbon array, related to G band, due to heteroatom doping into the carbon framework. Like the boron doping effect on the formation of structural defects,\(^{12,13,28,42,71}\) phosphorus doping results in an increase of defects composition in graphitic carbon material and the decrease of the crystallinity of graphitic structure.\(^{8,77}\)

The ratio of BDG900 is slightly higher than that of PDG700. This difference describes that BDG900 has more disordered defect sites than PDG700 despite having a larger covalent radius of the phosphorus, which causes critical defects in phosphorus-doped carbon. This phenomenon can be attributed to difference of the doping level between PDG700 and BDG900. The doping level of BDG900 obtained by quantitative analysis of wide XPS spectra is around 4.4 times higher than that of PDG700.

More defect sites of BDG900 can contribute to providing more reaction sites for the oxygen reduction. This contribution can be proof of the higher \textit{ORR} performance of BDG900 over PDG700, which will be discussed further.
**Figure 4-18.** Raman spectra of PDG700 and BDG900.
4.2.5 X-ray photoelectron spectroscopic (XPS) study

The wide XPS survey spectra show the presence of C, O, P, or B (Figure 4-19) in PDG700 and BDG900. The atomic concentration of C, O, P, or B is given in the Table 4-5. Importantly, sample calcined at 700 °C has only phosphorus (0.18 at.%), not boron (0 at.%); however, sample calcined at 900 °C possesses boron (0.82 at.%), not phosphorus (0 at.%). Naming of samples, PDG700 (phosphorus-doped graphene) and BDG900 (boron-doped graphene), is depending on a kind of heteroatom doped. From the result of one-sided doping of phosphorus or boron, the possibility selective doping depending on pyrolysis temperature is demonstrated. This phenomenon suggests easy tuning of types of heteroatom doped into carbon materials by varying pyrolysis temperature without any consideration regarding precursor and other synthetic conditions.

In PDG700, phosphorus 2p (P2p) peak is observed at a binding energy of 132.1 eV, which is positively shifted compared to a binding energy of pure P2p peak (129.7 eV). Similarly, in BDG900, boron 1s peak, observed at 189. 8 eV, is found to be positively shifted compared to binding energy of pure B1s peak (187 eV). These shifts of binding energies are ascribed to incorporated P or B into the graphene.8,13,15

From XPS quantitative analysis, the ratio of doped P into C (P/C) for PDG700 and doped B into C (B/C) for BDG900 are found to be 0.19% and 0.87%, respectively. The heteroatom to C ratio of BDG900 is around 4.5 times higher than that of PDG700 even though atomic concentrations (%) of P and B are same in the precursor. This situation can be explained by covalent radius effect.78 Incorporation of P atom into the carbon network is more difficult than introduction of B atom because of greater covalent radius of P atom (110 pm) than that of C atom (77 pm), compared to similar covalent radius of B atom (88 pm) to C atom.

After deconvolution of high resolution P2p spectrum, the P2p spectra on PDG700 are separated into two components, as shown in Figure 4-20 (a). For PDG700, the highest binding energy at 133.7 eV is assigned to P-C bonding. The peak at 132.0 eV is due to P-O bonding. From deconvoluted B1s peak on BDG900 are divided into four components, which are the same.
components as BDCs discussed in Chapter 4.1. The peak with the highest binding energy at 192.5 eV is derived from BCO$_2$. The peak observed at 190.7 eV is owing to BC$_2$O. The peaks centered at 188.7 eV and 186.7 eV correspond to BC$_3$ and B$_4$C, respectively. The binding energy values for the two components of P2p and the four components of B1s are closely matched to advanced research results with the same tendency. The instances of B1s peak deconvolution were introduced in previous discussion. For examples of P2p peak deconvolution, Liu et al. reported that the peaks of P-C and P-O bonding were detected at a binding energy of 130.3 eV and 132.7 eV in phosphorus-doped graphite layers. Liu et al. observed that the peaks of P-C and P-O were found at a binding energy of 130.3 eV and 132.2 eV, respectively. Analysis of the high resolution P2p and B1s spectra demonstrates that the carbon frameworks of both PDG700 and BDG900 are electronically modified by P or B atom doped, respectively.
Figure 4-19. Wide XPS spectra of PDG700 and BDG900.

Table 4-5. Composition of C, O, P, and B in PDG700 and BDG900 based on Figure 4-19 and 4-20

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic percent (at.%)</th>
<th>Phosphorus or boron distribution (at.%)</th>
<th>P/C or B/C ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C  O  P  B</td>
<td>P-O  P-C  BCO₂  BC₂O  BC₃  B₃C</td>
<td></td>
</tr>
<tr>
<td>PDG700</td>
<td>95.28  4.54  0.18  0</td>
<td>62.9  37.1  0  0  0  0</td>
<td>0.19</td>
</tr>
<tr>
<td>BDG900</td>
<td>94.16  5.02  0  0.82</td>
<td>0  0  13.3  58.2  11.8  16.7</td>
<td>0.87</td>
</tr>
</tbody>
</table>
Figure 4-20. High resolution XPS spectra of (a) P2p of PDG700 and (b) B1s of BDG900.
4.2.6 Electrochemical study

1) Cyclic voltammetric studies

The cyclic voltammograms (CVs) of untreated pristine graphene show an unclear cathodic peak at 0.65 V vs. RHE with a peak current of -0.99 mA cm\(^{-2}\). On the other hand, PDG700 and BDG900 exhibit a well-defined oxygen reduction cathodic peak at 0.66 V and 0.71 V vs. RHE with a peak current of 1.61 mA cm\(^{-2}\) and 1.78 mA cm\(^{-2}\). These are around 1.5 to 2 times higher than that of the untreated graphene. In addition, the current density difference between the background and reduction curve at 0.7 V vs. RHE was compared among the prepared samples and the graphene. The value of untreated graphene is found to be 0.73 mA cm\(^{-2}\). However, the values of PDG700 and BDG900 are determined to be 1.61 mA cm\(^{-2}\) and 1.78 mA cm\(^{-2}\), and these are 2.2 to 2.4 times higher than that of the graphene. The above results indicate that heteroatom doping enhances oxygen reduction current due to electronically modifying the pristine graphene by incorporating heteroatom into the graphene array.

The most positive onset potential of the three samples is observed at 810 mV vs. RHE in CVs of BDG900. This value of BDG900 is 30 mV more positive than that of the untreated graphene. This observation indicates that BDG900 enhances the oxygen reduction kinetics of the graphene better than PDG700. In turn, this finding indicates that boron doping of BDG900 results in faster kinetics of the ORR with high current density. The evidence for this difference of the contribution between PDG700 and BDG900 will be introduced in a latter section of the paper with hydrodynamic linear sweep voltammograms (LSVs) using RDE technique. ORR performance comparison between PDG700 and BDG900 will also be discussed in these latter sections.

2) Rotating disk electrode (RDE) technique

In LSVs on PDG700 and BDG900, current density increases with an increase of the electrode rotation speed from 400 rpm to 2500 rpm, as shown in Figure 4-22 (a) and (b). The corresponding K-L plots in
Figure 4-22 (c) and (d) show great linearity and good parallelism. The linearity and parallelism of the plots indicates first-order kinetics and constant electron transfer over a wide potential range. In particular, all K-L plots of both prepared samples are found to have similar slope to ideal K-L plots when electron transfer is four, which suggest that both prepared samples follow four-electron pathway for oxygen reduction.

ORR performance was enhanced by increasing the pyrolysis temperature from 700 °C to 900 °C, which is the same tendency as BDCs discussed in Chapter 4.1. Figure 4-23 shows the comparison of the ORR activity among PDG700, BDG900, and Pt/C, which is obtained under the same experimental conditions as comparison LSVs among BDCs and Pt/C. The various kinetic parameters derived by K-L equation (Eq. 2.4) are shown in Table 4-7. The calculated n values of PDG700 and BDG900 are 3.98 and 3.94, while the values for pristine graphene are 2.1 to 2.7, as reported by Sheng et al. These results suggest that heteroatom doping into the graphene has the possibility to induce single-step four-electron transferred oxygen reduction like Pt-based catalysts.

The onset potentials of PDG700, BDG900 are found to be 0.78 V and 0.82 V, which is similar to the values observed in CVs. Although the onset potentials of the prepared samples are more negative than that of Pt/C, BDG900 cause 40 mV positive shift of the onset potential compared with the pristine graphene. This shift is also close to the results obtained in CVs.

In comparing PDG700 and BDG900, BDG900 shows higher oxygen reduction performance than PDG700. This difference is ascribed to differences of defect concentration related to sp\(^3\) disordered carbon between the two samples. The doping concentrations of PDG700 and BDG900 are different although synthetic precursor that possesses simultaneously P and B with same atomic concentration was used for pyrolysis. The higher doping concentration of BDG900 results from much easier doping of boron due to the similar covalent radius of boron with carbon atom rather than the doping of phosphorus into the carbon network. As mentioned previously, the difference of doping level induced more defect sites in samples that can act as harsh reaction sites. Namely, the presence of more reaction sites for ORR in BDG900 contributed to the higher electrocatalytic activity of the ORR.
Figure 4-21. Cyclic voltammograms of (a) PDG700, (b) BDG900, and (c) pristine graphene. Dotted line for N₂-saturated 0.1 M KOH and solid line for O₂-saturated 0.1 M KOH.

Table 4-6. ORR activity of PDG700, BDG900, and pristine graphene by CV technique

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset potential (V vs. RHE)</th>
<th>Peak current (mAc m⁻²)</th>
<th>Current density difference at 0.7 V vs. RHE (mAc m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDG700</td>
<td>0.77</td>
<td>-1.61</td>
<td>1.61</td>
</tr>
<tr>
<td>BDG900</td>
<td>0.81</td>
<td>-1.78</td>
<td>1.78</td>
</tr>
<tr>
<td>Graphene</td>
<td>0.78</td>
<td>-0.99</td>
<td>0.73</td>
</tr>
</tbody>
</table>
Figure 4-22. Hydrodynamic linear sweep voltammograms (LSVs) of the ORR on (a) PDG700 and (b) BDG900 in 0.1 M KOH at 10 mVs\(^{-1}\) at various electrode rotation speeds. Corresponding K-L plots of (c) PDG700 and (d) BDG900.
Figure 4-23. LSVs of the ORR on PDG700, BDG900, and Pt/C in 0.1 M KOH at a scan rate of 10 mVs\(^{-1}\) at 1600 rpm.

Table 4-7. Electrocatalytic parameter for the ORR of PDG700, BDG900, and Pt/C by hydrodynamic linear sweep voltammetry

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset potential (V vs. RHE)</th>
<th>Electron transfer (n) at 0.3 V vs. RHE</th>
<th>Kinetic current density (J(_k)) at 0.7 V vs. RHE (mAc㎡)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDG700</td>
<td>0.78</td>
<td>3.98</td>
<td>1.80</td>
</tr>
<tr>
<td>BDG900</td>
<td>0.82</td>
<td>3.94</td>
<td>5.50</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.98</td>
<td>3.98</td>
<td>28.08</td>
</tr>
</tbody>
</table>
4.2.7 Selectivity and durability study

1) Selectivity study: methanol oxidation tolerance and CO poisoning test

In Figure 4-24 (a), (c), and (e), selectivity for ORR evaluated by methanol tolerance test is depicted for PDG700, BDG900, and commercial Pt/C. The solid line was obtained in O₂-saturated electrolyte, and the dotted line was obtained in methanol added O₂-saturated electrolyte. The solid line and the dotted line in LSVs of PDG700 and BDG900 closely overlap; however, the dotted line in LSV of Pt/C is not matched significantly and forms a gap with the solid line. This gap observed in LSVs of Pt/C corresponds to the oxygen reduction current decay due to simultaneous methanol oxidation, and strongly suggests the outstanding methanol tolerance of PDG700 and BDG900.

The results of CO poisoning effect on the oxygen reduction are illustrated in Figure 4-24 (b), (d) and (f) for PDG700, BDG900, and Pt/C, respectively. The solid line was attained in O₂-saturated electrolyte, and the dotted blue line was obtained in both CO and O₂-saturated electrolyte. To consider a decrease in O₂ partial pressure owing to the addition of CO gases, the dotted red line was obtained in both N₂- and O₂-saturated electrolyte. For PDG700 and BDG900, the dotted blue line and the dotted red line are closely matched. On the other hand, the blue line and the red line in LSV of Pt/C show critical disparity. This disparity suggests that the oxygen reduction on commercial Pt/C electrode can be affected by CO poisoning while PDG700 and BDG900 show strong resistance against CO poisoning.

(2) Durability test

Figure 4-25 depicts the relative current decay of Pt/C electrode to 64.8%. On the contrary, PDG700 and BDG900 exhibit greater durability than Pt/C. The relative currents of PDG700 and BDG900 decline to 87% and 89%, respectively. This finding describes that both PDG700 and BDG900 have long-term stability in ORR in alkaline medium.
Figure 4-24. LSVs with addition of 2 M methanol on (a) PDG700, (c) BDG900, and (e) Pt/C. LSVs with addition of CO (blue line) and N\textsubscript{2} gases (red line) at the same flow rate as O\textsubscript{2} gas on (b) PDG700, (d) BDG900, and (f) Pt/C in O\textsubscript{2}-saturated 0.1 M KOH solution at 1600 rpm.
Figure 4-25. Chronoamperometric response of PDG700, BDG900, and Pt/C at -0.26 V vs. SCE in O$_2$-saturated 0.1 M KOH solution for durability test during 12 h (43200 s).
V. Conclusion

In conclusion, we have introduced a simple and cost-effective pyrolysis approach for the fabrication of BDCs, PDG700, and BDG900 as non-precious catalysts for oxygen reduction. This synthetic approach is a single step using a single precursor without templates, solvents, or catalysts. Particularly, the control of pyrolysis temperature was found to have roles in the tuning doping level in BDCs and the selecting kind of heteroatom doped into the parent carbon network in the study of PDG700 and BDG900.

The BDCs, PDG700, and BDG900 exhibited comparable performance with commercial Pt/C (E-TEK) for ORR in alkaline medium. Electrocatalytic performance improved when the temperature of pyrolysis was increased from 700 °C to 900 °C. Improved electrocatalytic performances of BDC900 and BDG900 are attributed to the presence of BC₃ composition and defect sites in the catalysts more than BDC700 and PDG700, respectively. The durability of BDCs, PDG700, and BDG900 electrode was better than that of the commercial Pt/C catalyst under continuous oxygen reduction. In addition, BDCs, PDG700, and BDG900 electrode was completely inactive for methanol, CO oxidation, whereas commercial Pt/C electrode was prone to deactivation because of methanol oxidation and CO poisoning.

The results strongly suggest that the doping heteroatom and the tuning of the doping level could be a rational approach for non-precious and metal-free catalysts for oxygen reduction. This study suggests that the simple synthetic approach is applicable to design and fabricate heteroatom-doped materials for various catalytic applications. Furthermore, if investigation of oxygen reduction mechanism on boron or phosphorus-doped carbon-based materials is accompanied by computational calculation, this study will be powerful method to advance commercialization of alkaline fuel cells.
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요 약 문

이종 원소가 도핑된 탄소재료를 이용한 알카라인 연료전지 Cathode 용 산소환원 촉매의 합성 및 평가

알카라인 연료전지에서 산소환원반응이 일어나는 cathode 의 백금촉매를 대체하여 연료전지 제작 비용 감소에 기여하고자 비백금 촉매를 합성하였다. 촉매의 합성에 이용된 solid-state pyrolysis 은 단일 전구체로부터 단일 process 를 거쳐 탄소격자 내에 이종 원소를 치환도핑하는 손 쉬운 기술이다. 또한 별도의 templates, solvents, catalysts 가 필요하지 않으며, 대량생산에도 용이하게 적용될 수 있다는 점에서 이용가치가 있다.


전기화학적 특성평가로부터, BDC900 과 PDG700 및 BDG900 은 알카라인 전해질에서 백금과 같이 4 전자 산소환원반응을 촉진하며 commercial 백금촉매와 경쟁할 수 있는 산소환원능력을 가짐을 알게 되었다. 지속적인 산소환원반응 하에서의 내구성과, 메탄올 crossover 및 CO 피독작용에 대한 저항성은 백금촉매를 압도하였다. 이러한 결과는, 기존의 백금촉매를 대체하여 연료전지 전체 제작비용을 감소시킴으로써, 연료전지의 상업화에 기여할 가능성을 제시한다. 또한 탄소격자 내 이종 원소 도핑 및 solid-state pyrolysis 기술은 광범위한 촉매 분야로의 무한한 적용가능성을 시사한다.

핵심어: 이종 원소 도핑 탄소, 전기화학적 촉매, 산소환원반응, 알카라인 연료전지, 비백금 촉매
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**Journal:**

**Domestic conference:**

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