



Hierarchically porous heteroatom-doped carbon derived from flue gases for electrochemical energy storage



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ABSTRACT

This study investigated the synthesis of hierarchically porous heteroatom-doped (B and N) carbon materials from CO₂ or flue gas by CO₂ conversion using NaBH₄ as a reducing agent and their applications as supercapacitors. The resultant carbon materials exhibited a high specific capacitance of 210 F/g at 1 A/g, which is higher than that found in a typical activated carbon. This is because their hierarchical micro-mesoporous structure causes ions to diffuse into the carbon pores with low resistance. In particular, the process synthesizing B/N dual-doped carbon from flue gas reduces the capital/operating cost because the process does not involve an energy-intensive separation process of CO₂ from flue gas. Therefore, the direct conversion of flue gas into B/N dual-doped carbon can lead to a sustainable practice of CO₂ utilization.

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1. Introduction

Carbon dioxide (CO₂) emission arising from the use of fossil fuels is a critical issue due to its detrimental effects on global warming. Sixty percent of CO₂ emission in flue gas is from industrial power plants operated by fossil fuel combustion [1]. Because industrial flue gas mixtures from coal-fired power plants contain up to around 15% of CO₂ [1], the global warming effect can be significantly reduced if CO₂ is captured through effective physical or chemical processes. The efforts to reduce the CO₂ include capturing CO₂ from flue gas using membrane with ionic liquid [2], and converting CO₂ to methanol using an electrochemical method [3]. Additionally, CO₂ can be an abundant, inexpensive, and non-toxic carbon source. For these reasons, various CO₂ conversion and capture techniques have been investigated to reduce their emissions and global warming. Among the CO₂ treatment processes, CO₂ conversion has received great interests because greenhouse gases can be reutilized, and essential chemical products can be obtained by the process.

Recently, CO₂ transformation into porous carbon materials has gained attention due to their electrochemical applications as electrode materials [4–7]. Various CO₂ conversion approaches have

been proposed to produce carbon nanotubes (at 70 MPa) [4], porous carbon (at 32 MPa) [5], and even graphene (use of dry ice) [6]. However, the severe reaction conditions require a significant amount of energy to convert thermodynamically stable CO₂ which may cause much more energy consumption and CO₂ emission. To save more energy, Zhang et al. used an appropriate reducing agent, sodium borohydride (NaBH₄), to convert CO₂ into porous carbon at atmospheric pressure and 500 °C [7]. Additionally, boron (B) in NaBH₄ can be incorporated in the carbon framework during CO₂ reduction [7]. Heteroatom-doped carbons in the electrochemistry fields generally improve the electrochemical performances of their non-doped analogues [8].

Even though CO₂ conversion into carbon materials is quite a promising process, all of the previous studies mentioned so far used pure CO₂ [4–7] which requires high-cost CO₂ separation and purification processes from the flue gas before CO₂ conversion. Thus, more efficient CO₂ conversion methods are required to reduce the process operating cost. This study attempted to use flue gas as it is without any CO₂ pre-capture to produce useful porous carbon materials. The conversion was done with NaBH₄ as a reducing agent.

Various porous carbons are suitable and useful for supercapacitor applications as electrode materials due to their unique properties, such as a high electrical conductivity, high surface area range, and controlled pore structure [9–12]. In particular, hierarchically porous carbons, defined as carbon materials in

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which different nano-scaled pores (micro/meso/macro) are interconnected, allow more efficient diffusion of ions into the pores, leading to capacitance enhancement in supercapacitor applications [13–18]. Hence, if carbon materials derived from CO₂ or flue gas exhibit hierarchically porous structures with high surface areas, the carbon production processes do not only reduce the representative greenhouse gases but also produce highly efficient electrode materials for supercapacitors.

In this study, hierarchically porous carbon materials were produced from a reaction of CO₂ or synthetic flue gas with NaBH₄ as a reducing agent followed by the KOH treatment to increase their surface area. Boron-doped carbon (BC) derived by CO₂ was activated with different BC/KOH ratios (1:1–1:3) at 850 °C. Interestingly, the varied BC/KOH ratios led to different portions of micro, meso and macro pores. Even though the BC activated with a 1:3 ratio of BC/KOH exhibited the highest BET surface area (2771 m²/g) and highest specific capacitance (236 F/g at 1 A/g), BC activated with the same amount of KOH (1:1) showed the highest specific capacitance per unit surface area, (0.137 F/(g m²) at 1 A/g) due to its higher portion of meso/macropores. Thus, boron/nitrogen dually doped carbon (BNC) obtained from synthetic flue gas was treated with a BNC/KOH ratio of 1:1 at different activation temperatures. The BNC activated at 850 °C with KOH exhibited 22% higher specific capacitance (at 1 A/g) than the KOH-treated BC at the same temperature with the same ratio of carbon to KOH (1:1). This increased capacitance is from further N-doping from N₂ in flue gas that makes the carbon framework more hydrophilic facilitating the penetration of the electrolyte.

2. Experimental

2.1. Materials

CO₂ (purity:>99.8%), N₂ (purity:>99.9%), and Ar (purity:>99.9%) were supplied by Deokyang Co., Ltd. Sodium borohydride (NaBH₄, purity:>99%) was obtained from Sigma-Aldrich. Potassium hydroxide (KOH, 90% for the activation step and 99.99% to make 6 M KOH electrolyte for electrochemical tests), hydrochloric acid (HCl, 37 wt% in water), and polytetrafluoroethylene (PTFE, 60 wt% dispersion in water) were obtained from Sigma-Aldrich. Ethanol (EtOH, purity:>94.0%) was obtained from Daejung Chemicals & Metals Co., Ltd. (Korea). All of the chemicals were used without further purification. Deionized (DI) water was produced with a Millipore Direct-Q unit with a resistivity of 18 MΩ cm⁻¹.

2.2. Preparation of B- or B/N-doped porous carbon by CO₂ or flue gas conversion

NaBH₄ was placed in a boat-type alumina crucible, and it was put inside the alumina tube mounted in a tube-type electric-furnace (GSL1100X, MTI Co.). The air existing in the alumina tube was purged with CO₂ or a synthetic flue gas mixture composed of 85% N₂ and 15% CO₂ for 1 h. CO₂ or the flue gas mixture was continuously supplied into the tube (at 70 cm³/min, atmospheric pressure) during the following temperature-varying process. The tube temperature increased up to 500 °C for 100 min, and the temperature was held for 2 h to produce BC samples using CO₂ or for 3 h to produce BNC samples using the gas mixture, and then, the system was cooled down to room temperature. Likewise, the same samples were synthesized by 4 repeated runs, and all of them were finely powdered. The resultant products were put into 450 mL of DI water and agitated for 4 h at 95 °C to dissolve the Na₂CO₃ and NaBO₂ which are the byproducts of the reaction [7]. After vacuum-assisted filtration of the solutions, this process was repeated four times. The carbon products were further washed with EtOH. The carbon product was filtered again and dried in a vacuum oven at

80 °C at less than 0.1 bar for 24 h. Then, the samples were dispersed in 30 mL of a 5 M HCl solution and agitated for 3 h. The solutions were held for 2 h to precipitate the carbon materials. The carbon materials were washed with DI water until the pH reached 6–7 and then, washed again with 300 mL of ethanol. The remaining ethanol in the pores of the carbon sample was evaporated in the oven at 80 °C. The carbon samples derived from CO₂ and the flue gas mixture without the KOH treatment were named BC10 and BNC10, respectively. Additionally, for comparison with KOH-activated BNCs, BNC10-850, which was heat-treated at 850 °C under Ar without the KOH treatment, was prepared.

2.3. KOH activation of BC and BNC

BC and BNC obtained in the previous step were dispersed in the KOH-dissolved ethanol and sonicated for 1 h. The ratios of BC to KOH were 1:1, 1:2, and 1:3. In the case of BNC, the ratio of the carbon material to KOH was only 1:1. After drying all of the samples to evaporate the ethanol, they were further dried in a vacuum oven at 80 °C and at less than 0.1 bar for 24 h. The samples were put in a boat-type crucible that was placed inside an alumina tube. Before the heat treatment, the air in the tube was purged by Ar for 1 h at 50 cm³/min. Then, the temperature of the tube, in which the BC was placed, was increased to 850 °C at a heating rate of 5 °C/min and maintained at this temperature for 2 h. In the case of the BNC treatment, the tube temperature was heated to 700, 850, or 1000 °C at the same heating rate and time. After the KOH activation of the carbon samples, the tubes were cooled down to room temperature. All of these processes were done under 0.1 MPa of Ar at 50 cm³/min. The resultant carbon products were washed through the same procedure as mentioned in 2.2. The KOH-treated BCs at 850 °C were named BC11-850, BC12-850, and BC13-850 depending on the carbon-KOH ratio. Additionally, KOH treated BNCs with a carbon-KOH ratio of 1:1 were named BNC11-700, BNC11-850, and BNC11-1000 depending on the treatment temperature (700, 850, and 1000 °C).

2.4. Characterization

X-ray photoelectron spectroscopy (XPS) data were acquired using a MultiLab 2000 (Thermo) system equipped with Al Kα radiation (hν = 1486.6 eV) as a probe. The chamber pressure was 5 × 10⁻¹⁰ mbar, and the size of the analysis spot was 500 μm. The spectra were referenced to the C1s peak at 284.5 eV. Powder X-ray diffraction (XRD) measurements were done with a D/MAX-2500 X-ray (Rigaku) diffractometer for a 2θ range of 10–80° at a scan rate of 2°/min and a step size of 0.02° using graphite monochromatic Cu Kα (λ = 1.5406 Å) radiation with a nickel filter. The tube current was 300 mA with a tube voltage of 40 kV. Scanning electron microscope (SEM) images were acquired with a Magellan 400 (FEI) field emission microscope. Electron-dispersive X-ray spectroscopy (EDX) analysis was performed with an accelerating voltage of 5.0 kV at a magnification of 5 k X, and the content of the elements on the surface was calculated. The BET surface area (BET) was determined by N₂ adsorption-desorption isotherms at 77 K from TriStar II 3020 (Micromeritics). The pore size distribution was derived from the BJH theory. The micropore volume (V_{micro}) was determined with the Dubinin-Astakhov equation.

2.5. Electrochemical measurements

All electrochemical measurements were done with a three electrode system using an electrochemical station of Potentiostat/Galvanostat/EIS (VSP, BioLogic) with EC-Lab[®] software V10.34. The carbon slurries were prepared by mixing the BC or BNC samples (23 mg) as active materials and polytetrafluoroethylene (PTFE,

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