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Enhanced electrocatalytic reduction of oxygen at CO_2-derived Fe—N—B-doped porous carbon

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ABSTRACT

Fe—N—B doped carbon catalysts are synthesized directly from flue gas containing CO_2. They showed enhanced activity for oxygen reduction reaction in an alkaline electrolyte (1 M NaOH), which is comparable activity of commercial platinum catalysts. The amorphous carbon contains nitrogen species derived from nitrogen gas in flue gas and boron atoms which were originated from the reducing agent of sodium borohydride for the flue gas conversion. The amounts of iron species was controlled from 5% to 55% of synthesized amorphous carbon from flue gas. The sample with 33% of Fe precursor species shows the highest oxygen reduction reaction activity. This is due to the existence of pyridinic nitrogen doping and Fe—N bonding in the carbon network verified by X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) analyses. Also, from the microscopic images, the degradation of oxygen reduction reaction activity comes from agglomeration of Fe species. The Fe—N—B—C catalyst shows the promise of stability in acidic conditions and long-term durability for 10,000 cyclic voltammetric cycles.

1. Introduction

The polymer electrolyte fuel cell (PEMFC) is known to provide higher energy and power density than supercapacitor or lithium ion battery [1]. However, the development into a wide application is hindered because platinum is expensive and the cost is subject to the variable market. More platinum catalyst is needed in the cathode for oxygen reduction reaction (ORR) than the anode with hydrogen evolution reaction because of sluggish kinetics of ORR. To avoid using expensive platinum-based electrocatalysts for ORR, non-precious metal catalysts containing transition metal or metal oxide, have attracted much attention [2]. By using metal macrocycles like Fe or Co-phthalocyanine and porphyrin with Fe—N bonding, the ORR activity has been improved significantly [3–5].

One representative example includes the Fe—N/C catalyst synthesized from the mixture of Fe salt, g-C_3N_4 and carbon sources like graphene and carbon nanotube (CNT) via heat treatments [6,7]. Those attempts used reduced graphene oxide (rGO) or CNT as a carbon source.

This work, however, presents the direct utilization of flue gas as a carbon source to firstly synthesize the Fe—N—B—C composite. The synthesized Fe—N—B—C catalyst showed a clear relationship between Fe—N/C ratio and ORR activity by surface chemistry as well as correlation between catalyst agglomeration and ORR activity. In addition, in the process of converting carbon dioxide, the boron doping also occurred due to using a boron-containing reductant of $NaBH_4$ [8,9]. The boron-containing carbon material is known to increase ORR activity because boron atoms act as electron-deficient active sites in B—C bonding for ORR [10,11].

Instead of using carbon dioxide alone [12–14], we utilized flue gas because if pure CO_2 is to be used for the CO_2 conversion, it needs an additional separation step of CO_2 from flue gas which requires high energy consumption [15,16]. Another purpose of using flue gas is that nitrogen is enriched in flue gas and N-doping may be possible in the presence of the reduction agent [17–19]. Thus, this study shows real potentials of making use of carbon dioxide directly from flue gas into the Fe—N—B—C electrocatalyst.

2. Materials and methods

2.1. Materials

CO_2 with a purity of > 99.8% and N_2 (99.9%) was purchased from Deokyang Co. Ltd. $NaBH_4$ with a purity of > 96% (from Sigma-Aldrich) and NaOH (95%) were acquired from Fisher Scientific. Hydrochloric acid (HCl, 37 wt% in water) was supplied by Sigma-Aldrich.

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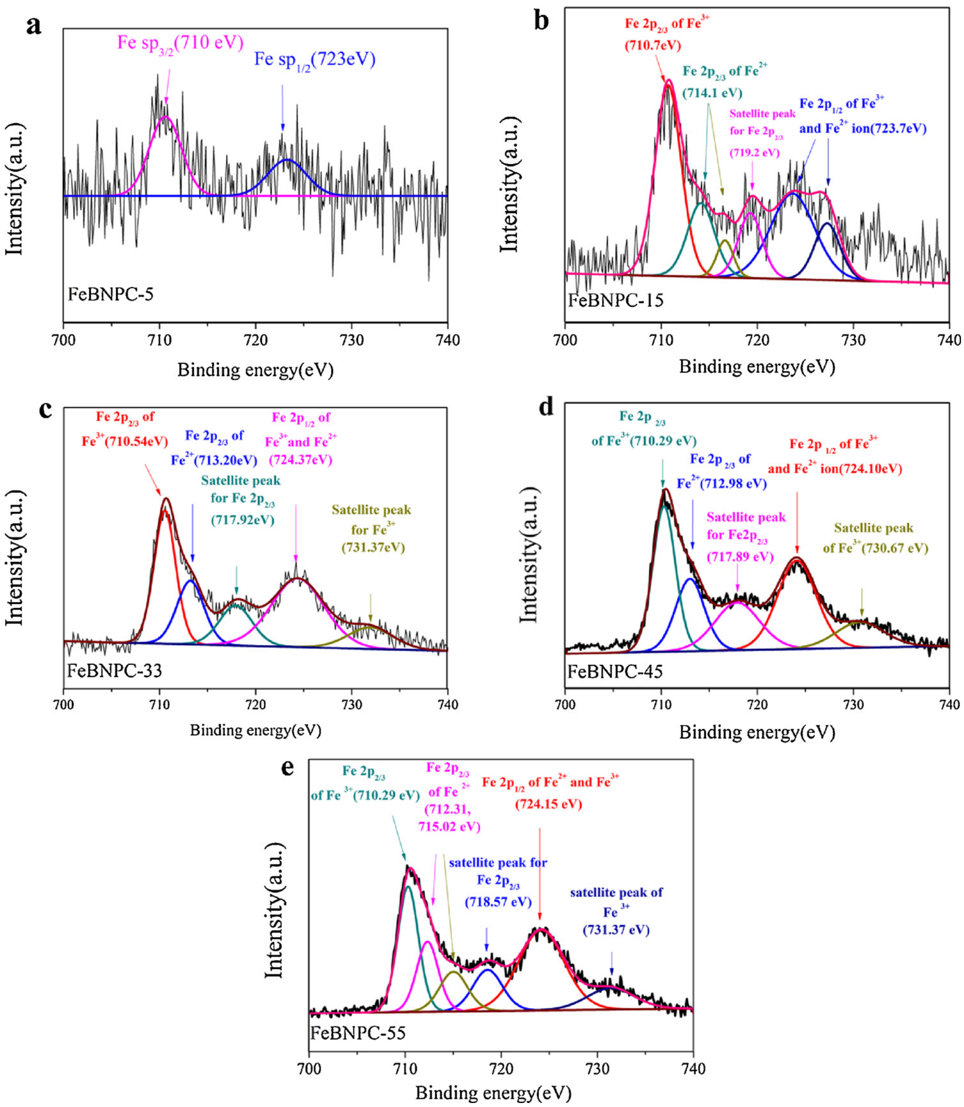

Fig. 1. XPS Fe2p spectra of FeBNPC-5(a), FeBNPC-15(b), FeBNPC-33(c), FeBNPC-45(d) and FeBNPC-55(e).

Polytetraflouoroethylene (PTFE) (60% dispersion in H_2O) was obtained from Sigma-Aldrich. Concentrated sulfuric acid (H_2SO_4, 95–98%) was used from Fluka. All chemicals were used as received without further purification. Deionized (DI) water was produced in our lab and had a resistivity of 18 MΩ cm^{-1}. Platinum (20 wt. % Pt loading) on graphitized carbon (Vulcan XC72) was acquired from Sigma-Aldrich.

2.2. *Flue gas transformation*

After loading $NaBH_4$ into an alumina crucible boat, and the boat was then put into a horizontal quartz tube mounted inside a furnace (GSL1100X, MTI Co.). The quartz tube was heated to 500 °C from room temperature in 100 min (5 °C/min), followed by maintaining at this temperature for 3 h, and finally cooled down to room temperature under a model flue gas (15% CO_2 and 85% N_2) of CO_2 with a flow rate of 10 cm^3 STP min^{-1} and N_2 with a flow rate of 57 cm^3 STP min^{-1} (0.1 MPa). To see conversion efficiency of real flue gas, the other gas mixtures of 80% of N_2, 15% of CO_2 and 5% of O_2 (or 13% CO_2, 73% N_2, 5% O_2, and 9% H_2O) were used to selectively convert CO_2 with a flow rate of about 70 cm^3 STP min^{-1} (refer to the supporting information). The solid products stored in a glass vial at ambient conditions.

2.3. *Treatment of solid product (formation of BNPC-500)*

The solid product obtained from the furnace experiments of flue gas transformation was put into a 250 cm^3 glass bottle (PYREX®), followed by addition of 80 cm^3 of DI water and heated at 95 °C with stirring at 260 rpm for 4 h, resulting in a suspension of fine particles. After withdrawing the clear supernatant, 80 cm^3 of DI water was added. This process was repeated four times and filtered, washed with DI water and ethanol and dried overnight in an oven at about 120 °C. Then, the solid sampled was called as BNPC-500.

2.4. *Formation of FeBNPCs*

BNPC-500, which was from the product of the selective CO_2 conversion from the flue gas of 85% N_2 and 15% CO_2 by $NaBH_4$ at 500 °C, was dispersed in the DI water. After that, urea (four times of BNPC-500) and appropriate amounts of $FeCl_3$ (5–55 wt. % relative to BNPC-500) were also put into the vial, followed by sonication for 15 min for dispersion of the particle and hydrolysis of urea. The solution was poured into an alumina crucible boat and dried at 120 °C overnight. After that the dried carbon materials were pyrolyzed in the tubular furnace at temperature of 850 °C under 50 STP min^{-1} of N_2 atmosphere. After the heat-treatment, the residual carbon was washed with hot DI water,