Control of nitrogen content and its effects on the electrochemical behavior of nitrogen-doped carbon nanofibers

Jiyoung Kim [a,b,*], Jin-Sung Jang [a,b], Dong-Hyun Peck [a,b], Byungrok Lee [b], Seong-Ho Yoon [c], Doo-Hwan Jung [a,b,**]

[a] Advanced Energy Technology and System, University of Science and Technology (UST), Yuseong-gu, Daejeon 305-333, Republic of Korea
[b] New and Renewable Energy Research Division, Korea Institute of Energy Research (KIER), Yuseong-gu, Daejeon 305-343, Republic of Korea
[c] Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

ARTICLE INFO

ABSTRACT

Nitrogen-doped carbon nanofibers (N-CNFs) with different nitrogen contents were synthesized from vaporized acetonitrile as a simultaneous carbon and nitrogen source via the chemical vapor deposition method. N-CNF synthesis was conducted at 640 °C for 2 h, and the ratio of nitrogen and hydrogen mixture as reactant gas was adjusted to control the nitrogen content in the N-CNFs. The amount of hydrogen in the reactant gas was varied in the range from 0 to 40 mL min^{-1}. The physical and electrochemical properties of the N-CNFs were characterized. The content of introduced nitrogen decreased with the ratio of supplied hydrogen, as opposed to the growth yield of the N-CNFs. Additionally, the nitrogen content and chemical states of the N-CNFs were examined and compared to reveal their correlations with the electrochemical behavior. The N-CNFs were found to have a noticeable electrochemical behavior such as capacitance and oxygen reduction reaction activity that was determined by the total nitrogen contents, especially those of pyridinic-nitrogen.

1. Introduction

Fuel cells have been widely developed for several decades and may potentially replace or assist several electrical applications. A huge obstacle for the commercialization of fuel cell technologies is the expensive price of the components such as catalysts, membranes or separate plates. Among them, the catalyst is a critical part to overcome the cost problem. Particularly, the sluggish kinetics of the oxygen reduction reaction on the cathode side induces the use of precious metals such as platinum or its alloyed form. Many studies have been conducted to overcome the cost difficulties through ways to increase the catalytic activity [1], enhance the durability [2] or develop non-precious catalysts [3,4]. For this reason, various forms of carbon have been formerly used as catalyst support materials. Nitrogen-doped carbons have been studied in various electrochemical devices such as sensors [5], batteries [6–9] and capacitors [10–13] owing to the unique reactivity of nitrogen in the carbon structure [14–17]. In particular, nitrogen-doped carbons

have been intensively applied as the electrode material of fuel cells due to attractive electrochemical behaviors [18–26].

Due to the wide range of researches on nitrogen-doped carbons for the past several years, there is no doubt that it appears significant activities for the oxygen reduction reaction under the influence of the nitrogen introduced into the carbon structure. It is well-known that the oxygen reduction reaction activity of nitrogen-doped carbon is determined by the total amount of introduced nitrogen or its chemical state, which is associated with nitrogen precursors or heat treatment conditions [27,28]. Also, the specific surface area and the porous structure are one of the important factors that determine the activity. Although many studies have been conducted, controversies about the real active states of doping nitrogen for intrinsic activity of oxygen reduction reaction are present. Pyridinic nitrogen has been generally considered as the main catalytic sites [27,29], but there remains the argument for higher activity in graphitic nitrogen [30]. Meanwhile, most of the studies were carried out in alkaline media, because, nitrogen-doped carbon has moderate ability for oxygen reduction in acid. On the other hand, nitrogen-doped carbon shows attractive performance comparable to the platinum in alkaline media due to the different oxygen reduction reaction mechanism depending on the electrolyte [31]. However, the fuel cell system, which is close to commercialization, is operated with acid electrolytes, so it is necessary to more deeply study the electrochemical behavior of nitrogen-doped carbon in acid state.

In presenting the paper, we attempt to control the nitrogen content in nitrogen doped carbons and to reveal the relations between the

* Correspondence to: J. Kim, Advanced Energy Technology and System, University of Science and Technology (UST), Yuseong-gu, Daejeon 305-333, Republic of Korea and New and Renewable Energy Research Division, Korea Institute of Energy Research (KIER), Yuseong-gu, Daejeon 305-343, Republic of Korea.
** Correspondence to: D.-H. Jung, Advanced Energy Technology and System, University of Science and Technology (UST), Yuseong-gu, Daejeon 305-333, Republic of Korea and New and Renewable Energy Research Division, Korea Institute of Energy Research (KIER), Yuseong-gu, Daejeon 305-343, Republic of Korea.
E-mail addresses: jyoung509@ust.ac.kr (J. Kim), doohwan@kier.re.kr (D.-H. Jung).

electrochemical behavior and introduced nitrogen. Nitrogen doped carbon was prepared from the same precursor and heat treatment condition. Also we selected the fiber structure, which most of the surface is exposed to the outside, to minimize the effect of porous structure on the oxygen reduction reaction activity, and attempt to evaluate the intrinsic active site of the nitrogen-doped carbon by dividing the performance as the specific surface area. In order to do so, the nitrogen-doped carbon nanofibers (N-CNFs) were directly synthesized via a catalytic chemical decomposition method over nickel-iron catalysts using vaporized acetonitrile at same synthetic temperature. Different amounts of hydrogen in the reactant gas were supplied to control the nitrogen content. The structural and electrochemical characteristics due to the introduction of nitrogen into the carbon structure were examined and discussed based on the experimental results in this study.

2. Materials and methods

2.1. Materials

Reagent-grade chemicals such as nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), citric acid and acetonitrile (CH_3CN) were purchased from Junsei Chemical Co., (Japan). Hydrogen (>99.999%) and nitrogen (>99.999%) were obtained from Special Gas (Republic of Korea) and were used after passing through a moisture trap.

2.2. Synthesis of N-CNFs

N-CNFs were synthesized via a catalytic CVD method over a nickel-iron catalyst on a magnesium-based support material [32,33]. A NiFe–MgO catalyst (molar ratio of Ni:Fe:Mg = 4:1:5) was prepared through the modified process of Chen et al. [34] and Pang et al. [35]. Prescribed amounts of each metal nitrate and citric acid were dissolved in distilled water. Then the solution was heated to evaporate the water completely, and yellow color ash product was collected and ground. The ash product was heat-treated at 180 °C for 2 h, further heat-treated at 350 °C for 1 h in air atmosphere. The finished solid catalysts showed brown color, and were ground again to use. The metal to magnesium oxide ratio was fixed at 1:1, and the nickel to iron molar ratio was 4:1.

N-CNFs were synthesized on 0.1 g of the NiFe–MgO catalyst in a horizontal tube furnace. The reactor was fully purged with nitrogen for 15 min prior to elevate the temperature for the synthesis. When the reactor reached 640 °C, the gas composition was changed to the designed value and 0.035 mL min^{-1} of acetonitrile was supplied in the vapor form through a 120 °C heater. The reaction of acetonitrile for N-CNFs on NiFe–MgO was carried out for 2 h, and then the reactor was naturally cooled down with nitrogen flow. The nitrogen contents in the N-CNFs were controlled by changing the compositions of hydrogen and nitrogen during synthesis at 640 °C. The N-CNFs synthesized under 160 mL min^{-1} of nitrogen flow and 40 mL min^{-1} of hydrogen
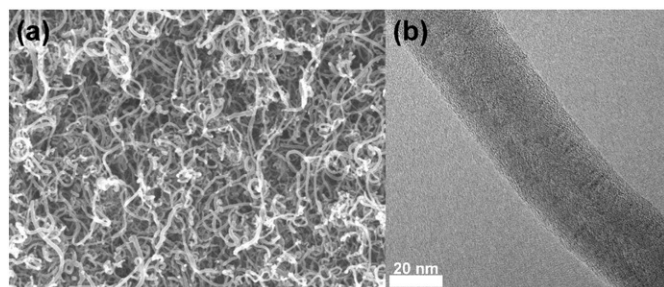
Table 1
Physical properties and nitrogen contents of the N-CNFs.

| | Yield (g_{CNF} h^{-1} g^{-1}_{cat}) | S_{BET} (m^2 g^{-1}) | d_{002} (nm) | N/(N + C) at.% | |
				EA	XPS
H00	1.09	88	0.340	7.59	12.45
H20	3.33	150	0.342	4.72	7.91
H30	3.67	159	0.344	4.33	6.29
H40	4.08	183	0.344	3.67	6.15
H40-HT	–	213	0.345	3.22	4.80

flow were referred to as H40. The hydrogen flow was reduced to 30 mL min^{-1} (with 170 mL min^{-1} of nitrogen) and 20 mL min^{-1} (with 180 mL min^{-1} of nitrogen), and the N-CNFs were referred to as H30 and H20, respectively. The H00 sample was synthesized under only nitrogen flow of 200 mL min^{-1}. In addition, the H40 sample was heat-treated in 800 °C for 2 h under nitrogen flow, which was named H40-HT.

2.3. Characterization of the N-CNFs

Morphologies and surface structure of the N-CNF were observed by scanning electron microscope (SEM, S-4700, Hitachi) and transmission electron microscope (TEM, Tecnai G2 F30, FEI). For TEM observation, very small amount of sample was dispersed in isopropyl alcohol and sonicated for 10 min. The well-dispersed carbon suspension was dropped onto a microgrid, and completely dried. The N-CNF yields were calculated as the residual amount from thermogravimetric analysis (TGA, STA409PC, NETZSCH). Sample carrier containing about 2 mg of the N-CNF was heated to 900 °C at a constant heating rate of 5 °C per minute under air flow. The total nitrogen content was obtained from elemental analysis (FLASH EA-2000, Thermo Scientific). The surface nitrogen content was evaluated via X-ray photoelectron spectroscopy (XPS, AXIS-NOVA, Kratos Ins.). The C1s spectra were examined in the range of 275 to 295 eV, and the N1s spectra were recorded in the range of 390 to 410 eV. The binding energy correction was calibrated to the C1s main peak energy at 284.53 eV. The nitrogen contents on the surface and its chemical states were calculated as the area ratio of the C1s and N1s peak deconvolutions. The structural properties such as the specific surface area were evaluated through nitrogen sorption measurements using a BELSORP-mini instrument (BEL JAPAN Inc.). Prior to measurement, the samples were completely degassed at 250 °C for 3 h under vacuum. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were analyzed using the Barrett–Joyner–Halenda (BJH) method. X-ray diffraction profiles were obtained using a RINT2000 instrument
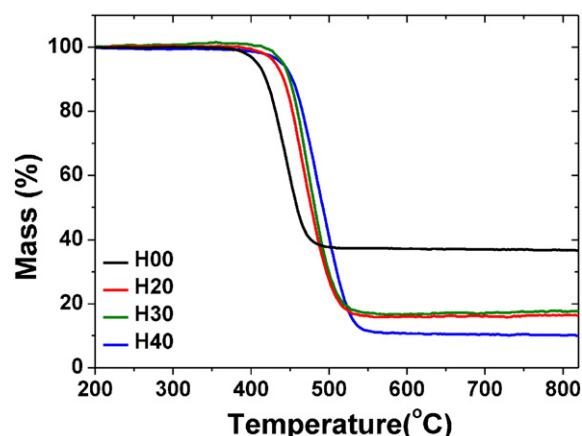

Fig. 1. SEM and TEM image of the N-CNF synthesized with 40 mL min^{-1} of hydrogen flow (H40) at 640 °C.

Fig. 2. Thermogravimetric profiles of the N-CNFs with a metallic catalyst.