Synthesis of N-doping carbon nanomaterials using thermal plasma-based methane pyrolysis

J.-H. Oh[1], Y. H. Lee[2], and S. Choi[2]

[1]*Electric Energy Research Center, Jeju National University, Jeju, Republic of Korea*
[2]*Faculty of Applied Eenrgy System, Jeju National University, Jeju, Republic of Korea*

Abstract: N-doping carbon nanomaterials were synthesized through thermal plasma-based methene pyrolysis. The effect of methane flow rate on morphology and N-doping of products was studied. As a result, The elemental analysis of products revealed a composition of 95.57 at% C, 2.74 at% N, and 1.69 at% O. It was identified that the products have an aggregate shape with a particle size of less than tens of nanometers.

Keywords: Thermal plasma, Methane pyrolysis, N-doping carbon.

1. Introduction

Carbon nanomaterials such as fullerenes, nanotubes, fiber, and N-doping have become one of the most exciting and rapidly growing areas of research in academia and industry. These have potential future applications due to their stable physicochemical properties, low cost, good conductivity, and high surface area or porosity [1]. The carbon nanomaterials manufacturing process is generally synthesized at high temperatures in the range of 1700-2500 K and is based on the reaction of a hydrocarbon feedstock to emit gaseous by-products such as H_2O, H_2, CH_4, and some pollutants, CO_2, SO_2, and NO_x[2].

Two methods have gained popularity in the synthesis of carbon nanomaterials: low-temperature heterogeneous graphitization with catalysts; and conventional high-temperature graphitization to form carbon well-developed graphitic order. The synthesis procedures employed to produce such materials are rather complicated. This technology requires a large investment and corresponding aerogel prepared by the sol-gel method from the polymerization of resorcinol with formaldehyde [3].

Recently, the CH_4 pyrolysis process using thermal plasma has been a notable technology because it has the signification advantage of producing carbon and hydrogen without CO_2. In general, the different plasma technologies used can be classified into two main categories, thermal plasma, and non-thermal plasma. Thermal plasma synthesis is an alternative method to reduce input energy and exhibits many advantages, such as low cost and high quality, because carbon synthesized by high-temperature graphitization is much more efficient.

The present work aims to synthesize N-doping carbon nanomaterials using thermal plasma-based methane pyrolysis. It is to synthesize N-doping carbon nanomaterials, which is a high value-added carbon, rather than general carbon. We conducted a synthesis experiment using a thermal plasma system with an adjusting methane flow rate. Characteristic analysis was performed for the products to confirm that they were doped with nitrogen.

2. Experimental setup

We suggest a synthesis method of N-doping carbon nanomaterials through a methane pyrolysis process. This process was based on DC thermal plasma torch. Fig. 1 shows a schematic diagram of DC thermal plasma system to synthesize N-doping carbon nanomaterials. This system consists of DC thermal plasma torch, power supply, cyclon filter, methane inlet, and graphite linear. Herein methane inlet position was possible to design close to the plasma torch exit to inject methane into the high-temperature region.

Operation conditions of DC thermal plasma system were summarized in Table 1. We adjusted the methane flow rate at a fixed flow rate of plasma-forming gas and input power. The nitrogen of plasma-forming gas was used as the N-doping source without additional reactive gas. Since energy provided per unit of gas determines the temperature of the plasma gas, methane flow rate and input power of plasma were chosen as affecting factors of methane conversion and N-doping in this study. We defied specific energy input (kJ/L) as power divided by methane flow rate. Equations are written as:

$$Specific\ Enrgy\ Input\ (SEI) = \frac{Input\ power}{Methane\ flow\ rate} \quad (1)$$

The morphology and elemental mapping of products were investigated using field emission transmission electron microscopy and energy-dispersive X-ray spectroscopy (FE-TEM, EDS, Talos F200X G2, Thermo Fisher Scientific, USA). The surface electronic states and atomic composition were analyzed by X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Scientific, USA).

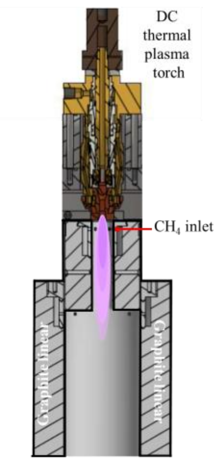

Fig. 1. Schematic diagram of DC thermal plasma system for the synthesis of N-doping carbon nanomaterials.

Table 1. Operating conditions for the synthesis of N-doping carbon nanomaterials from the thermal plasma-based CH_4 pyrolysis process.

No.	1	2	3	4
Plasma-forming gas flow rate (L/min)	Ar 4 + N_2 8			
Input power (kW)	7.7			
CH_4 flow rate (L/min)	5	10	15	20
Specific energy input (kJ/L)	92	46	30	23

3. Results and discussions

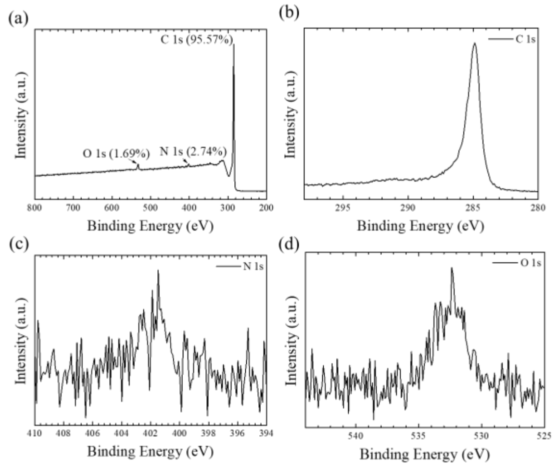

Fig. 2. XPS graphs of synthesized carbon nanomaterials from methane pyrolysis: (a) survey spectra, (b) C 1s, (c) N 1s, and (d) O 1s.

We conducted a synthesis experiment of N-doping carbon nanomaterials using a DC thermal plasma system. The chemical bonding of the products was analyzed by XPS, as indicated in Fig. 2. We identified the existence of C, N, and O elements from Fig. 2(a). Herein, the O element may be present due to air contamination as the samples were kept in the air for several days. The elemental analysis revealed a composition of 95.57 at% C, 2.74 at% N, and 1.69 at% O. Fig. 2(b~d) shows the high-resolution core-level spectrum. We estimated N-doping carbon was synthesized through XPS analysis.

Fig. 3 depicts the FE-TEM analysis images of the synthesized carbon nanomaterials. The products have an aggregate shape with a particle size of less than tens of nanometers. The components of products were further investigated through TEM-EDS mapping, as shown in Fig. 3 (b~d); the colors red, blue, and green correspond to elements carbon (C), Nitrogen (N), and Oxide (O), respectively. The TEM-EDS spectrum analysis identified an existence of 97.31 at% C, 1.44 at% N, and 1.26 at% O, as shown in Fig. 4. It considers the Cu spectrum of Fig. 4 occurs from TEM-Grid mesh made with Cu material. It was estimated that Nitrogen is doped into carbon through analysis results of XPS and FE-TEM. We estimated the synthesis mechanism of N-doping carbon nanomaterials using thermal plasma. The N atom or ion from N_2 dissociation reacts to C-H bonding species, generating CNH species as a precursor of N-doping carbon. This grows to solid carbon with dehydrogenation.

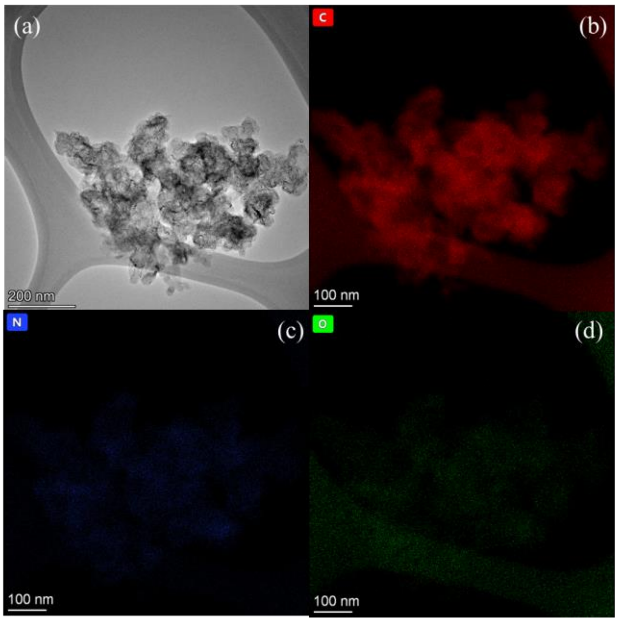

Fig. 3. FE-TEM analysis images of synthesized carbon nanomaterials from methane pyrolysis: (a) FE-TEM image, and (b~c) TEM-DES mapping images.

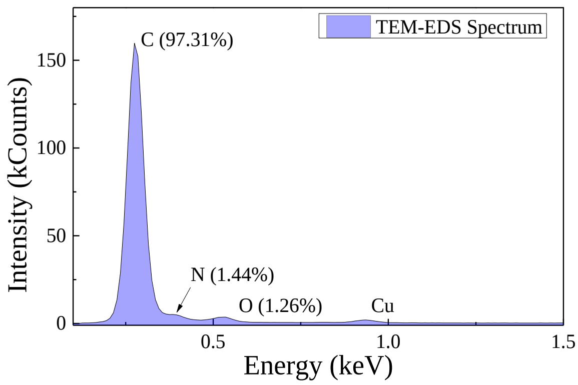

Fig. 4. TEM-EDS spectrum of synthesized carbon nanomaterials from methane pyrolysis.

4. Conclusion

We synthesized N-doping carbon nanomaterials using thermal plasma-based methan pyrolysis. It used the nitrogen of plasma-forming gas as the N-doping source without additional reactive gas. The characterization analysis revealed the existence of N in the synthesized carbon nanomaterials. In future work, we plan to apply synthesized N-doping carbon as the anode material of lithium-ion batteries. Also, the production of N-doping carbon nanomaterials will be improved by increasing the methane treatment capacity.

5. References

[1] D. L. Sun et al., Chemical Engineering Journal, **303**, (2016).
[2] F. Fabry et al., Chemical Engineering Science, **56**, (2011).
[3] X. Y. Liu et al., Powder Technology, **256**, (2014)
[4] M. Moreno-Couranjou et al., Carbon, **47**, 10 (2009).