Synthesis of carbon black as an anode material of lithium-ion battery using thermal plasma-based methane pyrolysis

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Abstract: Synthesis of functional carbon materials through methane pyrolysis using thermal plasma is significant for economic efficiency and CO_2 free. This work studied the synthesis of carbon black and hydrogen production in a one-step process. The synthesized carbon black was applied in an anode material of a lithium-ion coin cell. As a result, we identified that the capacity density decreased by more than 50% after 10 cycles.

Keywords: Thermal Plasma, Methane pyrolysis, Carbon black, Lithium-ion battery

1. Introduction

After the secondary battery is commercialized, graphite is mainly used as an anode material due to less structural change even during repeated charging and discharging and a long battery life with a stable capacity [1]. In general, coal tar from coal or petroleum is used as a raw material to produce graphite. Based on coal tar, coke is produced through a complicated process at a high temperature of 2,800 K-3,000 K. Then, artificial graphite is prepared by heat-treating coke at about 3,500 K. This method raises energy costs and carbon dioxide emissions, requiring an eco-friendly process. For this reason, thermal plasma processes are being developed, enabling a single process without pre-treatment or post-treatment.

Thermal plasma provides a high temperature of 1,000 K- 10,000 K and has a steep temperature gradient [2]. A large amount of methane can be decomposed in a short time. In addition, through the rapid cooling of the decomposed methane, by-products having higher crystallinity, electrical conductivity, and specific surface area than general carbon materials can be formed.

In this study, we synthesized eco-friendly carbon black in methane pyrolysis using thermal plasma. It can be synthesized in large quantities by methane pyrolysis in a one-step process. We evaluated the electrochemical properties of the synthesized carbon black assembled lithium-ion coin cell.

2. Experimental details

2.1 Synthetic experiment of carbon black

Fig. 1 shows a schematic of the DC thermal plasma system for methane pyrolysis and synthesizing carbon black. This system has a plasma torch, two graphite liners, a methane gas inlet, a quenching gas inlet, and a reactor.

Table 1. shows the details of the operating conditions of the DC plasma system. The experiment was carried out at atmospheric pressure, and the total input power was 30 kW using N_2 15 L/min as a plasma forming gas and a fixed current of 100 A. A graphite liner was installed inside to maintain the high temperature region further. In addition, methane was injected from 50 to 80 L/min, and a methane inlet point was installed in the middle of 1st graphite. This graphite structure helps to inject methane into the high temperature area and improve the methane conversion rate. The quenching gas was injected as a fixed 100 L/min. The crystal structure of the synthesized carbon black was analyzed using X-ray diffraction (XRD, Empyrean) using CuKα radiation (λ=1.5406Å). In addition, the crystalline and polymorphism of synthesized carbon black was analyzed using micro-Raman spectroscopy (LABRAM HR EV). The morphology and nanostructure of the synthesized carbon black was investigated with a field emission transmission electron microscope (FE-TEM, Talos) at an accelerating voltage of 200 kV.

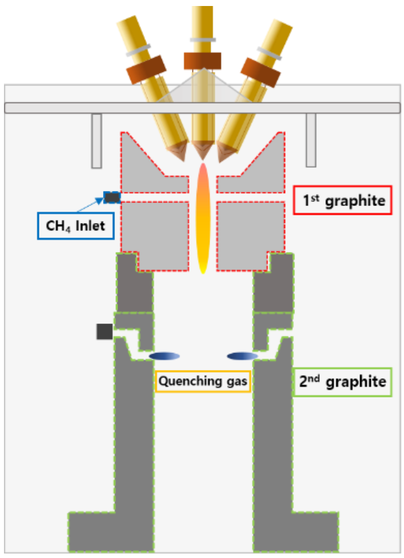

Fig. 1. Schematic of the DC thermal plasma system for methane pyrolysis.

Table 1. The operating conditions of DC thermal plasma system.

Total input power (kW)	30
Forming gas (L/min)	N_2 15
CH_4 injection (L/min)	50, 60, 70, 80
Quenching gas (L/min)	N_2 100
Operating pressure (kPa)	101.325

2.2 Electrochemical performance

A conductive material (SUPER-C65), sodium-carboxymethyl cellulose (Na-CMC) binder, and synthesized carbon black were used to make an electrode. The synthesized carbon black, the conductive material, and the binder were mixed with DI water in a ratio of 6:2:2 to make a slurry. The made slurry was spread to a copper foil of 250 µm using a doctor blade and then dried in a vacuum oven of 110℃ for 10 hours [3]. After the dried slurry was cut into a circular shape having a diameter of 15 mm, a CR2032-coin cell was assembled in an argon glove box using lithium as a cathode and 1M LiPF6 as an electrolyte. The assembled coin cell was tested by a battery tester (BTS-4000, Newware), which measured a voltage range of 0.01–3.0 V and an input current of 100 mA/g to see a change in capacity according to charging/discharging.

3. Result and discussion

Fig. 2 shows the XRD analysis results of the synthesized carbon black. The peak of the synthesized carbon black was similar at 22.6 °and 42.6 °, which are the peaks of commercial carbon black. It was confirmed that products form similar to commercial carbon black, and the change in the methane flow rate did not significantly affect the crystallinity of products.

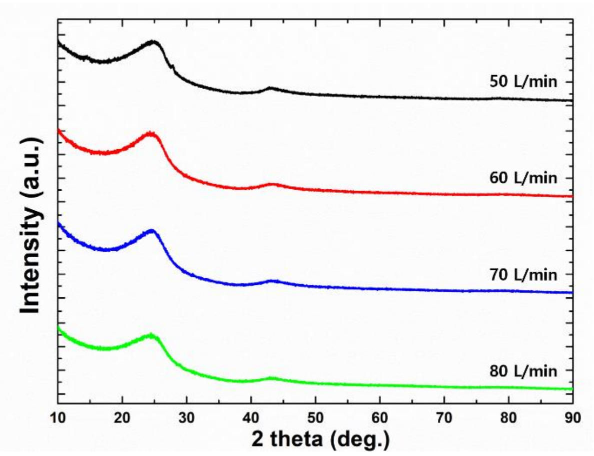

Fig. 2. XRD pattern of synthesized carbon black.

Fig. 3 Shows the Raman analysis data of the synthesized carbon black. Unlike ordinary commercial carbon black with a stronger or similar D peak than the G peak, it was confirmed that the synthesized carbon black has a strong G peak. Since it can be seen that the electrical conductivity is increased as the G peak is stronger in the Raman peak, it can be inferred that the electrical conductivity is higher than commercial carbon black but lower than graphite. In addition, when the methane injection rate increases, it can be seen that the G peak increases.

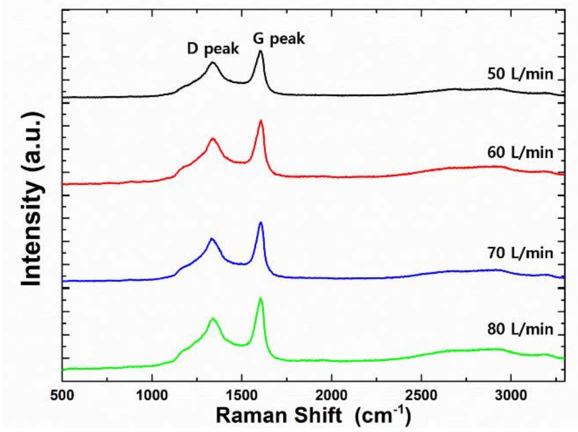

Fig. 3. Raman data of synthesized carbon black.

The morphology of the synthesized carbon black was analyzed using FE-TEM, as indicated in Fig. 4 The products show an average size of several tens of nanometers and a mixture of spherical and angular forms. And as the methane flow rate increases, the carbon black appears to be in an amorphous form.

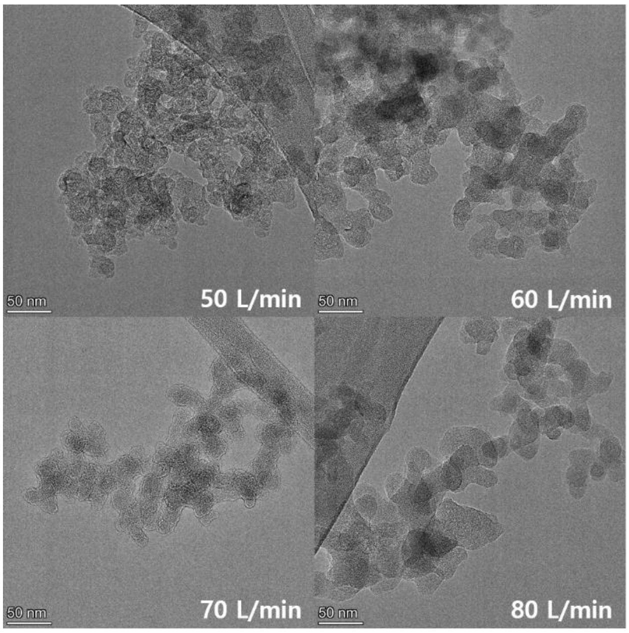

Fig. 4. TEM images of synthesized carbon black.

A charging/discharging test was conducted to evaluate the electrochemical properties of synthesized carbon black as anode material. Fig. 5 shows the results of a charge/discharge test of a coin cell made with synthesized carbon black. The initial discharge capacity was 304 mAh/g, lower than graphite's theoretical value of 372 mAh/g. The capacity of the cell decreases to various physically and chemically complex interactions immediately. It is estimated that the biggest reason is the active material's loss due to the SEI layer's formation and growth.

Table 2. shows the results of the charging/discharging test for each cell. The capacity reduction rate was calculated by substituting each cell test result into the capacity reduction rate equation. In all tests, after 10 cycles, the capacity decreased by more than 50%. The rapid decrease in capacity is that lithium failed to react with a pure carbon compound. It is estimated that the synthesized carbon black is a mixture of pure carbon and hydrocarbon forms. Therefore, it is estimated that the required reaction during the battery charging/discharging process has not been performed properly.

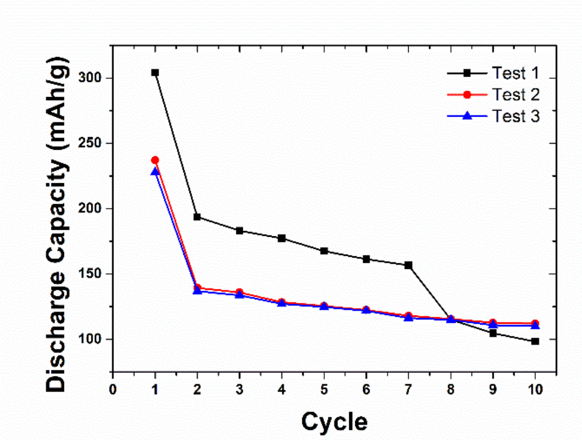

Fig. 5. Result of charge/discharge test of coin cell

Table 2. Capacity reduction rate for each cell test.

	First Discharge Capacity (mAh/g)	After 10 cycles Discharge Capacity (mAh/g)	Capacity reduction rate*
Test 1	304	98	0.67
Test 2	237	112	0.52
Test 3	227	110	0.51

* Capacity reduction rate : $\frac{10\ cycle\ capacity - first\ cycle\ capacity}{first\ cycle\ capacity}$

4. Conclusion

A carbon material was synthesized simultaneously with methane pyrolysis using a DC thermal plasma system. The synthesized carbon black is at the nano-size level and has a shape and characteristics similar to carbon black, but this has intermediate properties between graphite and carbon black. The synthesized carbon black has an amorphous morphology. As the methane inlet flow increased, the amorphous form increased, and it was confirmed that the G peak indicating graphitization, was slightly stronger. Cells made with the synthesized carbon black had an initial discharge capacity of 304 mAh/g, similar to commercial graphite. However, as charging/discharging progressed, the capacity significantly decreased by more than 50% after 10 cycles. It is estimated that the synthesized carbon black shows a rapid decrease in capacity because it is mixed with a hydrocarbon form unrelated to the reaction in the battery. A follow-up study will proceed to characterize whether these problems are related to the amount of methane inlet flow. After that, we will conduct follow-up experiments to find optimal conditions for methane pyrolysis and obtain high-quality carbon as a battery anode material.

5. References

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