Carbon Paper with a High Surface Area Prepared from Carbon Nanofibers Obtained through the Liquid Pulse Injection Technique

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ABSTRACT: To improve the performance of carbon paper used for applications such as electrodes for electrochemical devices and air filters, two types of long carbon nanofibers (CNFs) with average diameters of 20 and 49 nm were prepared by the liquid pulse injection (LPI) technique by adjusting reaction conditions. Carbon paper was made from the CNFs through a simple filtration process. The paper prepared from the CNFs with an average diameter of 20 nm (LPI-CNF(20) paper) was firm and flexible even though it was prepared without using any binders. LPI-CNF(20) paper also had a high surface area and showed a high electrical conductivity and a moderate gas permeability according to its void size. These properties are required for cathodes in the latest battery systems such as lithium–air batteries. In electrochemical experiments conducted to evaluate the performance of LPI-CNF(20) paper as a cathode, the paper showed a larger discharge capacity on the basis of the cathode weight than a conventional cathode (a commercially available carbon paper combined with a porous carbon), which indicated that it has a high potential to be used as a cathode in lithium–air batteries.

INTRODUCTION

Carbon papers (CPs) formed from carbon fibers (CFs) have several unique properties, such as a high electrical conductivity, a high mechanical strength, high gas permeability, and high chemical resistance. Hence, they are often used as current collectors for the latest energy storage/conversion systems, such as fuel cells and lithium–air batteries.1−5 When they are used in lithium–air batteries, they are generally coated with porous carbons using a binder, because their surface area is too small for surfactant reactions such as Li2O2 deposition to significantly proceed. In a typical preparation process of commercially available carbon papers, fibrous precursor polymers, whose diameters are several micrometers, are casted or woven into a paper and then the polymer paper is carbonized at a high temperature.6−7 As the surface area of such carbon papers depends on the diameter of the fibers composing it, it is difficult to increase the surface area when the diameter of the fibers is large. As a potential method to produce fibrous carbon precursors with a smaller diameter, the electrospinning method is known. Through this method, fibers having diameters from several micrometers to less than 100 nanometers can be obtained8−10 and such fibers can be easily casted into a paper. Because carbon fibers obtained from such fibrous polymers without heat treatment generally have an amorphous structure with turbostratic structure,11,12 their electrical conductivity is considered not to be as high as that of carbons composed of highly aligned graphene sheets. Therefore, papers constructed from fibrous carbons with such a highly aligned crystal structure and with a small diameter are preferable for various applications.

Carbon nanotubes (CNTs) are well-known fibrous carbons with small diameters and are formed by highly aligned graphene sheets. The diameter of CNTs is generally below 10 nm, which is much smaller than that of CFs, and the walls of CNTs are composed of a few layers of stacked graphene sheets. Because of their unique structure, CNTs have a large surface area (the theoretical surface area of single-wall CNT is around 1300 m2/g), a high electrical conductivity, and show a high chemical resistance. When CNTs are casted into a paper, they can be used as high-performance electrodes in electrochemical devices.13,14 In previous studies of lithium–air batteries, CNT paper showed a very high discharge capacity when used as a cathode.15

CNTs are generally prepared through chemical vapor deposition (CVD), where gaseous carbon sources flow into a heated reactor with metal nanoparticles located inside; CNTs elongate through the catalysis of the nanoparticles. In general, metal nanoparticles with appropriate sizes are supported on a substrate prior to CNT production.16 Although CNTs with small diameters and a highly aligned crystal structure can be prepared through this method, their productivity is not so high because this process is basically a noncontinuous “batch” process. Therefore, CNT paper tends to be extremely expensive. Generally, the required surface area in electrodes for various battery systems is not so high.17,18 Therefore, papers with only moderate surface areas are thought to be preferable, if
they are much more inexpensive than papers produced using CNTs.

To prepare such fibrous carbons, a modified CVD method has been developed, where the precursor of metal nanoparticles, usually an organometallic complex like ferrocene, is continuously provided along with the carbon source into the reactor. The precursor is heated in the reactor and decomposes, releasing numerous metal atoms. These metal atoms aggregate and form metal nanoparticles. They contribute to the formation of primary fibrous carbons, and then carbon layers are deposited on the catalytically formed primary fibrous carbons through thermal deposition of the carbon source. By using this method, fibrous carbons can be continuously produced but the diameters of the carbons through this method tend to be larger than those of CNTs. The diameter of fibrous carbons obtained through this method is usually several tens of nanometers to several hundred nanometers, so the fibers are usually called carbon nanofibers (CNFs). However, it is difficult to prepare CNFs with a high aspect ratio through this method because the catalyst life of the generated metal nanoparticles tends to be extremely short. Therefore, the obtained CNFs are thought not to be suitable for preparing CNF papers due to their limited aspect ratio. As it is difficult to reduce the diameter of the resulting CNFs in this method, it is essential to produce longer CNFs at a high productivity to prepare papers from CNFs.

To efficiently produce CNFs with long lengths, the liquid pulse injection (LPI) technique was developed. In this method, the initial source, which is a mixture of the catalyst source and the carbon source, is injected as a liquid pulse into a heated reactor. As soon as the solution makes contact with the heated wall of the reactor, the pulse is vaporized and the catalyst source in it instantaneously decomposes, releasing numerous metal atoms, as heat transfer between the solid wall and the liquid pulse rapidly proceeds. The metal atoms quickly coagulate and form fine metal nanoparticles. Fiber growth initiates as the nanoparticles make contact with the carbon source and reach the appropriate temperature. As this method enables the generation of highly active nanoparticles in a highly dense state, a large amount of long and uniform fibers can be produced at a high yield. Graphene sheets composing the wall of the obtained CNFs are well arranged in parallel to the axis of the fiber. Therefore, the CNFs obtained through this method are thought to have a high electrical conductivity. In addition, the diameter of the CNFs can be easily controlled, as the amount of thermal deposition of the carbon source can be regulated by adjusting the initial source composition and the carrier gas flow rate. The long and thin CNFs prepared through the LPI technique are expected to be easily castable into the form of a paper, and the resulting CNF paper is thought to be suitable for the electrode of batteries due to the high electrical conductivity of the CNFs which compose it.

In this work, we prepared CNFs with different diameters through the LPI technique and prepared paper from them to investigate how the diameter and length of CNFs affect the properties of the resulting carbon paper. The evaluated properties were surface area, gas permeability, and electrical conductivity. Furthermore, to demonstrate its high potential as an electrode, we conducted discharge tests using the CNF papers as the cathode in lithium–air batteries.

RESULTS AND DISCUSSION

CNFs with different diameters were prepared by adjusting reaction conditions in the LPI technique to investigate the effects of the thickness of CNF on properties of the CNF paper.
Figure 1 shows scanning electron microscope (SEM) images of the two types of LPI-CNFs, commercially available CNFs and a carbon paper (CP). Note that the commercially available CNFs and CP were, respectively, chosen as a sample which has a fiber diameter comparable to that of the LPI-CNFs and a sample which is generally used for the current collector in batteries. The diameters of the two types of LPI-CNFs are significantly different, as shown in Figure 1a,b. Therefore, the diameter of LPI-CNFs was successfully controlled by shortening the reaction time and by decreasing the concentration of the carbon source in the initial solution by using methanol as a diluent, which suppresses the deposition of carbon layers on the fibers. Their average diameters were calculated using SEM images and were 49 and 20 nm, respectively. Using these values, the LPI-CNFs will be denoted as LPI-CNF(49) and LPI-CNF(20) hereafter. As the aspect ratio of the obtained LPI-CNFs is extremely high, their lengths cannot be determined from SEM images. The high aspect ratio of the obtained CNFs can also be indirectly confirmed from the insets shown in Figure 1; the appearance of the LPI-CNFs is cotton-like, whereas the commercially available CNFs appear to be of a powder form. The commercially available CNFs have a diameter similar to that of LPI-CNF (20) (Figure 1c), and therefore the difference of their appearances suggests that the LPI-CNFs are much longer than the commercially available CNFs. Figure 1d shows an SEM image of CP. The diameter of the CFs composing the CP can be determined as ca. 9 μm, which is much larger than that of CNFs. Considering their smaller diameters, LPI-CNF(20) and LPI-CNF(49) are expected to show higher surface areas than those of the CFs composing CP. Therefore, papers prepared from them are expected to be suitable for the cathode in lithium−air batteries.

The prepared fibers were casted into a paper through a filtration process, where the fibers were first dispersed in toluene and then simply filtered out using a membrane filter. Figure 2a shows a photograph of a sample prepared from commercially available CNFs. The sample still looks powdery even after the filtration process due to the short lengths of the CNFs used to make it and is easily fractured into pieces even when gently handled. Figure 2b shows a photograph of a sample prepared through the filtration process from LPI-CNF(49). It was also fragile and could not be completely peeled off from the membrane filter, but its structure was confirmed to be firmer than that of papers made from commercially available CNFs because the peeled LPI-CNF(49) was still aggregated in fragments with dimensions of several millimeters. This suggests that long fibers contribute to the strengthening of the paper prepared from them but the entanglements between the fibers are not sufficient to make self-standing paper. Next, the LPI-CNF(49) samples were reinforced by passing a poly(vinylidene difluoride) (PVDF) binder solution through them after filtration. A typical reinforced sample is shown in Figure 2c and will be referred to as LPI-CNF(49)/PVDF paper hereafter. LPI-CNF(49)/PVDF paper was so firm that it could be pinched with tweezers without falling apart, indicating that it may have enough strength to be applied to electrodes for batteries. Paper samples were also prepared from LPI-CNF(20), as shown in Figure 2d. The obtained samples (LPI-CNF(20) paper) were self-standing even though they were synthesized without using any binders and could be handled easily without damaging their structure. This would be because LPI-CNF(20) easily get entangled with each other due to their diameter and/or their length. Considering that the difference of the diameters of LPI-CNF(20) and LPI-CNF(49) is not so large, their length may be significantly different. Moreover, LPI-CNF(20) paper can be...
folded without being fractured (Figure 2e), a feature that even CP (Figure 2f) does not have. Such a flexible paper is expected to be applicable to various applications.

Figure 3a,b shows N\textsubscript{2} adsorption isotherms and pore size distributions of LPI-CN\textsubscript{F}(20) paper, LPI-CN\textsubscript{F}(49)/PVDF paper, and CP at 77 K and (b) pore size distributions obtained by the Barrett, Joyner and Halenda method.

All of the isotherms show low uptakes in the low relative pressure region, around \( P/P_{0} = 0 \), which indicates that the samples hardly have micropores and their surface areas are attributed mainly to the external surface of fibers. Their Brunauer–Emmett–Teller (BET) surface areas \( (S_{\text{BET}}) \) were calculated and are listed as shown in Table 1. \( S_{\text{BET}} \) of CP (0.9 m\textsuperscript{2}/g) is much lower than those of LPI-CN\textsubscript{F}(20) paper (200 m\textsuperscript{2}/g) and LPI-CN\textsubscript{F}(49)/PVDF paper (19 m\textsuperscript{2}/g) because the diameter of the carbon fibers constructing CP is extremely large. From the diameters determined from SEM images, the surface areas of LPI-CN\textsubscript{F}(49)/PVDF paper and LPI-CN\textsubscript{F}(20) paper can be estimated as 43 and 106 m\textsuperscript{2}/g, respectively. Considering the LPI-CN\textsubscript{F}(49)/PVDF paper, the difference between the estimated surface area and the BET surface area is thought to be due to the bundling of fibers and/or clogging of voids by the binder. Considering the LPI-CN\textsubscript{F}(20)/PVDF paper, the BET surface area is larger than the estimated surface area, which is thought to be due to surface roughness. As only a moderate surface area is required in cathodes for lithium–air batteries, it is expected that both LPI-CN\textsubscript{F}(49)/PVDF paper and LPI-CN\textsubscript{F}(20) paper can be used for this application. Moreover, the \( N_{2} \) uptake of LPI-CN\textsubscript{F}(20) paper increased at a high relative pressure of \( P/P_{0} \approx 1 \), which indicates that LPI-CN\textsubscript{F}(20) paper has many voids between the fibers which compose it, whose sizes are comparable to meso- and macropores, as confirmed from its pore size distribution shown in Figure 3b. In cathodes for lithium–air batteries, such meso- and macropores are mainly used for \text{Li}_2\text{O}_2 deposition during the discharge process.\textsuperscript{18,26,27} Hence, a high capacity is expected when LPI-CN\textsubscript{F}(20) paper is used as the cathode in lithium–air batteries.

To utilize CNF papers as a catalyst support used in a flow system, electrodes for fuel cells, and lithium–air batteries, a moderate gas permeability is required. Hence, the gas permeability of the obtained CNF papers was evaluated through air flow experiments. Figure 4 shows the pressure drop that occurs when air is passed through the CNF papers at different linear velocities. The data of CP was also measured, but the results are not shown as the values were negligibly small. LPI-CN\textsubscript{F}(49)/PVDF paper shows a lower resistance than that of LPI-CN\textsubscript{F}(20) paper. This can be regarded as a reasonable result because the void size in CNF papers, which affects the resistance, depends on the diameter of the fibers that compose it. The size of the voids within the papers were estimated using the Hagen–Poiseuille equation, as shown in (eq 1).

\[
Q = \frac{\pi R^4 \Delta P}{8 \mu L} \tag{1}
\]

\( Q \): Linear velocity (m/s) \( \Delta P \): Pressure drop (MPa/cm) \( L \): Thickness of the paper sample.  
Figure 4. Results of gas permeability tests of LPI-CN\textsubscript{F}(49)/PVDF paper and LPI-CN\textsubscript{F}(20) paper with different flow rates.

| sample | \( S_{\text{BET}} \) (m\textsuperscript{2}/g) | estimated surface area (m\textsuperscript{2}/g)\textsuperscript{a} | porosity (%)\textsuperscript{b} | conductivity (S/cm) |
|--------|-----------------|----------------------|-----------------|------------------|
| LPI-CN\textsubscript{F}(49)/PVDF paper | 19 | 43 | 77 | 25 |
| LPI-CN\textsubscript{F}(20) paper | 200 | 106 | 83 | 179 |
| CP | 0.9 | 0.3 | 80 | 191 |

\( \text{a} \)Calculated from the fiber diameters observed from SEM images and true density of carbon (2.0 g/cm\textsuperscript{3}), assuming that all CNFs are uniform cylinders. \( \text{b} \)Calculated by the equation \( \varepsilon = 1 - \frac{4m}{\pi \rho_{c} d L} \) (\( \varepsilon \): porosity, \( m \): weight of the paper sample, \( \rho_{c} \): true density of carbon, \( d \): diameter of the paper sample, \( L \): thickness of the paper sample).

Table 1. BET Surface Areas, Porosities, and Electrical Conductivities of Samples
LPI-CNF papers were simply formed through filtration of preprepared CNFs, connections based on only physical contact exist between the CNFs that form them. Because of this, their electrical resistance is concerned to be higher than that of CP, which is produced by carbonizing a precursor paper constructed from a fibrous polymer. LPI-CNF(20) paper, however, shows a very high electrical conductivity comparable to that of CP. This is thought to be due to two reasons: LPI-CNF(20) is so long, so the number of highly resistant connecting points can be reduced, and the electrical conductivity of LPI-CNFs is higher than that of the CFs constructing CP because fibrous carbons prepared through CVD methods including LPI-CNFs generally show a high electrical conductivity due to the well-arranged graphene sheets composing them, even without an additional heat treatment. However, the electrical conductivity of LPI-CNF(49)/PVDF paper was lower than that of LPI-CNF(20) paper and CP, whereas the porosities of the three samples are comparable. This is because the insulating PVDF binder tends to reduce the number of the electrical paths within the paper. These results show that LPI-CNF(20) paper has sufficient electrical conductivity to be used as electrodes in batteries and it can also be used as a current collector like CP.

To evaluate the performance of LPI-CNF(20) paper as a cathode for lithium–air batteries, LPI-CNF(20) paper was electrochemically tested at a current density of 50 mA/(g-cathode) using a 2032 coin cell having small holes on the cathode cover, enabling O2 to diffuse into the cell. For comparison, CP and Ketjen black (KB) coated on CP (CP-KB) were also tested. Figure 5 shows discharge curves of LPI-CNF(20) paper, CP, and CP-KB. LPI-CNF(20) paper showed a high discharge capacity of 921 mAh/g, whereas that of CP was only 2.5 mAh/g. This is because LPI-CNF(20) paper has a high surface area and a moderate volume of voids where Li2O2 can be deposited. As for CP, the extremely small surface area hardly contributes to the deposition of Li2O2 in the discharge process. Because of this, CP is generally used for the cathode of lithium–air batteries after being combined with KB to increase the surface area available for Li2O2 deposition; CP-KB showed a very high discharge capacity on the basis of the weight of KB (about 6000 mAh/(g-KB) at 50 mA/(g-KB)). However, the amount of KB that can be loaded on CP (9.1 mg) is only 1.1 mg, as shown in Table 2, and hence the discharge capacity based on the cathode weight is not quite large. In Figure 5, the discharge capacity of CP-KB measured at a current density based on the cathode weight (50 mA/(g-cathode)) is 415 mAh/g, which is smaller than that of LPI-CNF(20) paper. The areal capacity of LPI-CNF(20) paper was calculated to be 5.5 mAh/cm², which is larger than that of CP-KB (2.1 mAh/cm²) and is comparable to that of a sheet made of 12 mg of single-walled CNTs (about 6.5 mAh/cm²@0.4 mA/cm²). In addition to these results, LPI-CNF papers have a high productivity because the LPI-CNFs that are used to synthesize them can be more efficiently prepared through the LPI technique than typical CVD methods and the paper itself can be easily synthesized through a simple filtration process without using any binders. Although only the initial performance of LPI-CNF(20) paper as a cathode has been evaluated in this study, the performance should be further improved by combining it with a suitable porous carbon. Considering their unique properties, LPI-CNF(20) paper is thought to be a promising material for being utilized not only in lithium–air batteries but also in other electrochemical devices.

**CONCLUSIONS**

Two types of CNFs having different average fiber diameters were separately prepared through the LPI technique by adjusting reaction conditions. From the LPI-CNFs with an average diameter of 20 nm, self-standing papers could be prepared through a simple filtration process. The obtained paper had a firm and flexible structure, with a high surface area of 200 m²/g, and showed a high electrical conductivity. Its electrochemical evaluation as a cathode in lithium–air batteries exhibited that it has a larger discharge capacity based on the cathode weight than a porous carbon CP. This result suggests that the LPI-CNF paper can be potentially used as a cathode in lithium–air batteries without additional porous carbons and binders. Moreover, considering the features of high surface area, high gas permeability, and high electrical conductivity, LPI-CNF papers are also expected to be used for other applications, such as filters for the electrostatic removal of pollutants from...
Figure 6 shows the experimental apparatus for CNF production. H₂ flow rate was set at 409 and 999 cm³/min when preparing LPI-CNF(49) and LPI-CNF(20), respectively. The reactor was heated until the temperature at its center position reached 1473 K. After cooling down to room temperature (RT), the generated CNFs were collected from the bottom of the reactor.

The obtained CNFs were wetted with a few drops of NMP and were kneaded for 3 min using a planetary mixer (AR-100, Thinky). The wet CNFs were suspended in toluene by ultrasonic irradiation. The suspension, in which the CNF concentration was 50 wt %, was vacuum-filtered with a hydrophobic poly(tetrafluoroethylene) membrane (pore size: 0.1 μm, Advantec). For preparing LPI-CNF(49)/PVDF paper, an excess amount of 0.01 wt % PVDF/NMP solution was passed through the CNF layer just after the filtration of the LPI-CNF(49) suspension. The obtained sample was dried at RT. The areal density of the resulting CNF papers was approximately 6 mg/cm².

Characterization. CNFs and CP were observed using a field-emission scanning electron microscope (JSM-6500F, JEOL). The porous structures of the samples were evaluated by N₂ adsorption isotherms. Gas permeability of the paper samples was evaluated by measuring the pressure drop that occurs when air was passed through the samples. For the measurement of pressure drops, the paper sample was fixed in a handmade cell, where the cross-sectional inner diameter was 11 mm. The flow rates of air were regulated in the range between 100 and 400 cm³/min. In the measurement of electrical conductivities, paper samples were cut into rectangles (10 mm × 20 mm) and both ends of them were fixed to current collectors with a conductive paste (Dotite D-500, Fujikura Kasei). Both ends were connected to a potentiostat (HA-151, Hokuto Denko). Different voltages were applied between the ends of the samples, and the resulting currents were measured to obtain I–V plots. From the slope of the I–V plots, the electrical conductivity of the sample was calculated.

Performance Evaluation as a Cathode for Lithium–Air Batteries. The performance of LPI-CNF(20) paper, CP, and CP-KB as a cathode for lithium–air batteries was evaluated. LPI-CNF(20) paper and CP were used without modifications. For CP-KB cathode preparation, KB was mixed with a 12% PVDF solution in NMP at a weight ratio of 19/1 (KB/PVDF) for 3 min using a planetary mixer (AR-100, Thinky). The obtained mixture was rubbed into CP. The KB-introduced CP was dried at 388 K under vacuum for 15 h and then punched out into circles with a diameter of 16 mm using a punching tool. The casted KB weight on the circular cathode was approximately 0.1 μg.

2032-type coin cells with small holes in the cathode cap for allowing O₂ diffusion were assembled in a glovebox filled with Ar. Lithium metal, a glass fiber filter (GF/A, Whatman), and a solution of CF₃SO₃Li in TEGDME (TEGDME/CF₃SO₃Li = 4:1, molar ratio) were used as the counter electrode, the separator, and the electrolyte, respectively. The cells were set in a gas-tight box into which oxygen was supplied at a flow rate of 10 cm³/min. They were discharged until 2.0 V vs Li/Li⁺ at a current density of 50 mA/g (0.3 mA/cm²) after 10 h of rest in an oxygen atmosphere.

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