Properties regulation of carbon paper
through incorporating lignin-based carbon nanofibers

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Carbon paper is commonly used as one of the electrode materials in batteries, where its main function is to serve as a conductive material, providing a channel for electron transport, and also helping to improve the conductivity and stability of the battery. Therefore, it is necessary to study how to improve the performance of carbon paper. This study aims to enhance the performance of carbon paper used in proton exchange membrane fuel cells (PEMFCs) by incorporating lignin-based carbon nanofibers (CNFs). We investigated the effects of different process flows, papermaking methods, and the addition amount of lignin-based carbon fibers on the performance of carbon paper. The research indicates that using the wet papermaking method and the process of electrospinning, impregnation and hot pressing, addition of lignin nanofibers, pre-oxidation, impregnation and hot pressing, and carbonization can yield carbon paper with the best overall performance. The tensile strength is 9.4 mPa, the flexural strength is 390 mPa, the air permeability is 1320 L/m²/s, and the resistivity is 15 mΩ/cm. This significantly improves its mechanical strength, air permeability, and electrical conductivity, making it a promising material for PEMFCs.

1. Introduction

Carbon paper has the advantages of low cost, excellent electrical conductivity, corrosion resistance, and high stability [1], and it is a key substrate material for the gas diffusion layer in proton exchange membrane fuel cells (PEMFCs) [2]. The preparation research of high-performance carbon paper has a profound impact on the further development of the gas diffusion layer of fuel cells [3]. Therefore, it is necessary to improve the strength of carbon paper, and the quality of carbon paper depends on its preparation process [4-6].

At present, the commercialized carbon paper in China is completely dependent on imports, and there is an urgent need to develop and research carbon paper products with independent intellectual property rights [7]. The performance of carbon paper is affected by the modification

methods of carbon fibers and the preparation process. The uniform dispersion of carbon fibers in carbon paper is crucial to the excellent electrical and mechanical properties of the carbon paper [8, 9]. Surface modification of carbon fibers is a common method to improve their dispersibility [10]. Kong [11]and others pretreated carbon fibers with deionized water and alkali solutions of different concentrations to improve the dispersibility of carbon fibers, and prepared carbon paper with tensile strength increased from 1.44 kN/m to 2.49 kN/m, and the resistivity decreased from 143.58 mΩ/cm to 68.10 mΩ/cm. They also increased the porosity, and these performance improvements are beneficial for the subsequent impregnation and carbonization of the carbon fiber base paper. Wu [12]and others used a phenolic resin solution with a concentration of 11% as the impregnating liquid, impregnated for 4 minutes, and prepared high-performance carbon paper with a resistivity of only 27.1 mΩ/cm and a tensile strength of 103.9 N/cm by hot pressing at a temperature of 160 °C and a pressure of 3.0 MPa for 20 minutes. In the preparation process, binders (such as polyvinyl alcohol) are often added to bond carbon fibers together to form carbon paper with certain strength, and the strength performance is further enhanced through the impregnation of phenolic resin and hot pressing [13-15]. The procedures of these methods are relatively complex and have their limitations, so there is a need for further optimization of methods to improve the performance of carbon paper.

Lignin is the most abundant natural biomass containing aromatic compounds, and as a high molecular weight compound, it is characterized by its heterogeneous and amorphous structure. It constitutes a significant portion of plant tissue. Due to its cost-effectiveness and biorenewability, lignin is considered a promising alternative material[16-18]. Lignin also has several advantageous properties such as being inexpensive, having a high carbon content, excellent thermal stability, degradability, high rigidity, and good antioxidant properties [19-22]. These characteristics enable the carbon nanofibers (CNF) prepared from lignin to be widely used in the energy field. For example, in electronic devices and new energy vehicles, etc. Therefore, with the rapid development of energy storage technology, flexible and portable energy conversion and storage devices have also attracted widespread attention [23, 24]. Polymers such as PAN, PEG, and PVA can serve as precursors for carbon fibers due to their carbon backbone. Among them, PAN is most commonly used as a precursor for carbon fibers due to its high carbon content and mechanical strength, but its high cost limits its widespread application [25]. Therefore, research on lignin as a substitute has become a focus of attention. For example, Jayawickramage [26]and others mixed PAN with lignin in different proportions and prepared carbon nanofiber electrodes with high surface area and high conductivity through electrospinning. The assembled supercapacitors have a high specific capacitance of 128 F/g. Cao and others studied a phosphating process modification method, modified and pre-oxidized carbonized acetic acid lignin (CA) to obtain high-performance lignin-based carbon fibers, and the assembled supercapacitors had a high specific capacitance: 346.6 F/gat 0.1 A/g. In addition, the assembled supercapacitors also have stable and high energy density, maintaining an energy density of 24.3 W/kg even at 4000 W/kg [27]. It can be seen that lignin, as a biodegradable carbon fiber precursor, has great application prospects.

This article uses lignin-based carbon fibers prepared by electrospinning to impregnate carbon paper under different process conditions, and tests their performance with the aim of high-value utilization of waste from the paper industry while improving the performance of carbon paper, laying a theoretical foundation for the application of carbon paper in the energy field.

2. Materials and methods

2.1 Materials

Alkine lignin (Mw: 500; Purity: 50%~55%; Xi'an Qiyue Biotechnology Co., LTD), acetic acid (AR; Shanghai Lingfeng Chemical Reagent Co., LTD), polyethylene oxide (PEO, AR; Shanghai Macklin Biochemical Co., LTD), carbon fiber (Toray Industries, Inc., Japan), polyvinyl alcohol (Shanghai Chenqi Chemical Technology Co., LTD), phosphoric anhydride (AR; Shanghai Macklin Biochemical Co., LTD), phenolic resin (AR; Shanghai Macklin Biochemical Co., LTD), carbon paper (A domestic manufacturer).

2.2. Experimental method
2.2.1. Process flow and process optimization process

Wrap the drum in the electrospinning machine with carbon paper and adjust the parameters for spinning [28]. Add carbon nanofibers: the addition amount is 5 wt%, 10 wt%, 15 wt%, 20 wt%; Pre-oxidation: Under an air atmosphere, the temperature is increased to 250 °C at a heating rate of 0.4 °C/min and kept warm for 1 hour to pre-oxidize the fibers; Carbonization: Under a nitrogen atmosphere, the temperature is increased to 600 °C at a heating rate of 3 °C/min and kept warm for 60 minutes for carbonization treatment. ; Impregnation and hot pressing: Prepare an ethanol solution with a mass fraction of 11% of phenolic resin, immerse the carbonized body in the solution, and then hot press at 3 mPa and 150 °C for 20 minutes. Arrange the operations in different sequences as different processes, as shown in Table 1.

Table 1. Three process sequences for incorporating carbon nanofibers into the base carbon paper.

Step/Process	APIC	ICAP	IAPIC
Step1	Addition of lignin nanofibers	impregnation and hot pressing	impregnation and hot pressing
Step2	pre-oxidation and carbonization	carbonization	addition of lignin nanofibers
Step3	impregnation and hot pressing	addition of lignin nanofibers	pre-oxidation and carbonization
Step4	carbonization	pre-oxidation and carbonization	impregnation and hot pressing
Step5			carbonization

2.2.2. Performance characterization
2.2.2.1. Mechanical properties

Mechanical property testing was conducted using a universal mechanical testing machine (KYD-2000NS, China). Tensile strength was measured according to the ASTM D828 test standards, with samples cut into rectangles (10×100 mm²) and loaded at a rate of 10 mm/min. Bending strength was measured using the three-point bending method, with a span maintained at 30 mm and a descent rate of 0.5 mm/min.

2.2.2.2. Permeability

The air permeability of the carbon paper was analyzed by using the FX3300 air permeability tester. Place the carbon paper on the table of the permeability tester and select the test area of 20 cm^2 and the test pressure of 400 Pa. Wait until the instrument readings stabilize, then record the data. Each sample should undergo at least three air permeability tests, and the average value should be taken to determine the sample's air permeability.

2.2.2.3. Specific resistivity

The resistivity of the carbon paper was measured with the RTS-8 four-probe tester. First, the resistivity range of the sample was estimated from the sample size, and the corresponding range was selected. Place the sample, press the probe down, and connect the current to the sample. The required test resistivity was calculated based on the size of the sample and the instrument parameters, and the potentiometer was adjusted to display the required test current on the host machine. Mode is then adjusted so that the host displays the test results. At least 9 points shall be tested and the average measured to determine the resistivity of the sample.

2.2.2.4. Micromorphology

The absolutely dry carbon paper samples were placed on a sample stage with conductive adhesive for gold sputtering for 1 minute, and then observed under an SU1510 tungsten filament lamp at a voltage of 15 kV.

3. Results and discussion

3.1. Selection of Process Flow APIC and ICAP

We have set up two control experiments, one for pre-oxidation and carbonization only, and the other for impregnation and hot pressing only, which are denoted as control1 and control2, respectively. In Fig. 1(b), it was found that the resistivity of carbon paper was very high when only pre-oxidized carbonization (Control1) was performed. The air permeability of 5500 L/m^2/s is due to its loose structure after carbonization, and its bending and tensile strength measurement. The APIC shown in Fig.1(b),(c) can also find that even in the process step of carbonization, the bending strength is only about 100 mPa, and the tensile strength and conductivity are lower than that of the carbon paper made by ICAP. Although it has a good air permeability, the carbonization of carbon paper base paper without soaking with phenolic resin and thermal pressing, will seriously damage its fiber structure, make its mechanical properties greatly reduced, and cannot be used. However, carbon paper impregnated with phenol resin (control2) and hot pressing and ICAP showed relatively stable performance, so ICAP was selected for subsequent experiments.
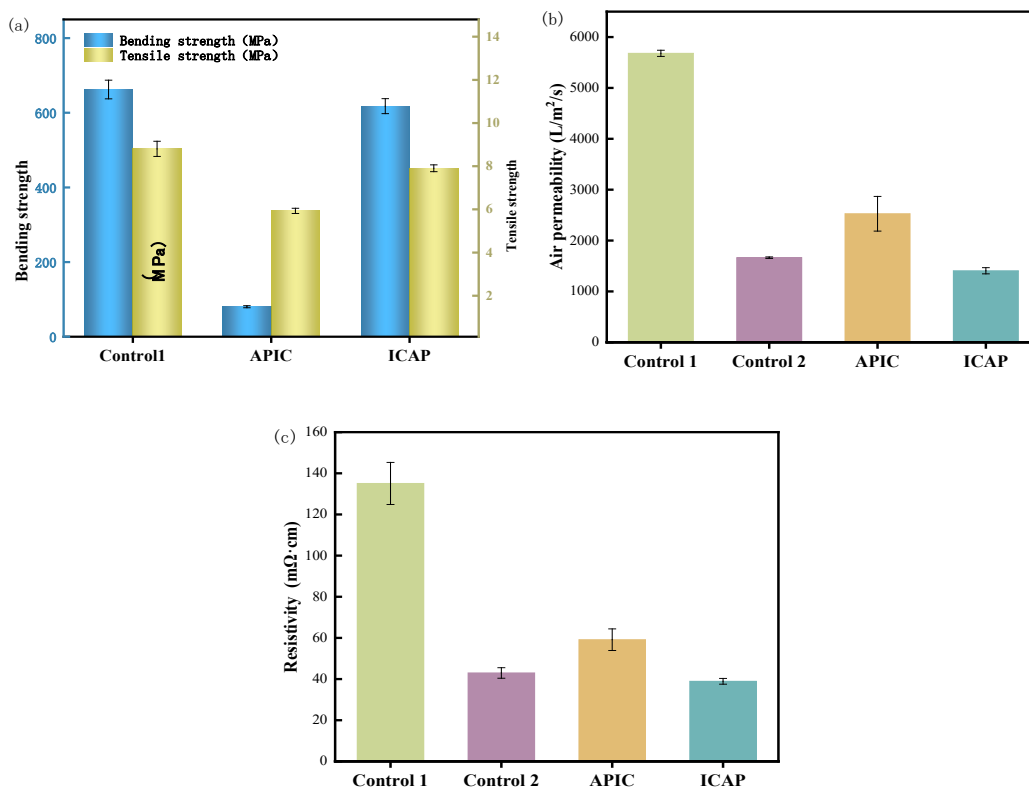
Fig. 1. Mechanical properties, air permeability, and resistivity of the control group, APIC, and ICAP.

3.2. Carbon paper properties made from process ICAP

As shown in Fig. 2, The bending strength shows a slight downward trend with the increase of the spinning amount., but almost the same, while the tensile strength of the carbon paper is not significantly associated with the change of the spinning amount. Therefore, the amount of CNF added by the ICAP, namely the spinning amount, has no obvious effect on the mechanical properties of the carbon paper.
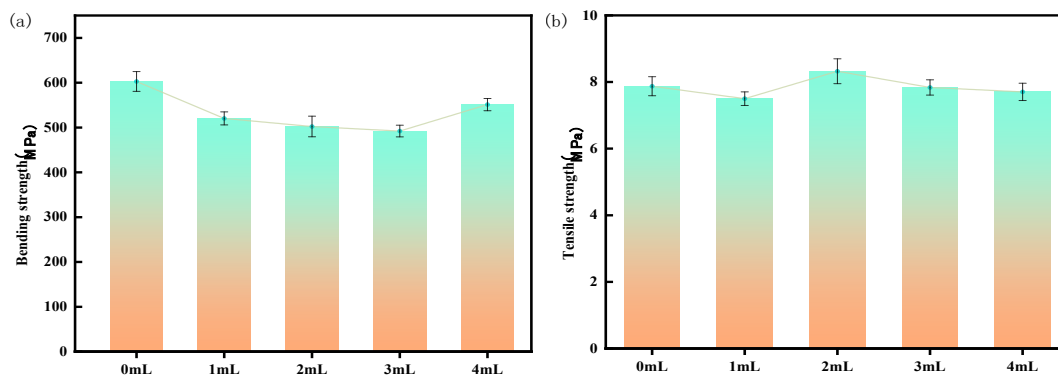
Fig. 2. Mechanical properties of carbon paper with different spinning amounts produced by process ICAP.
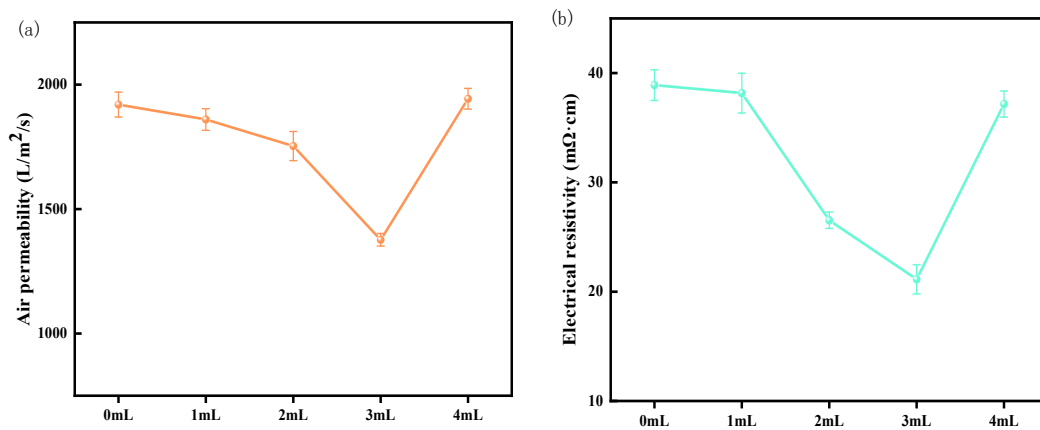
*Fig. 3. Air permeability and electrical conductivity of carbon paper
with different spinning amounts produced by process ICAP.*

In Fig. 3, the air permeability of the carbon paper decreased with the increasing spinning volume, most likely because the CNFs blocked the original pores of the carbon paper, especially when the spinning volume was 3 mL. At the same time, the resistivity of carbon paper is also reduced, when the spinning amount is 3mL, the resistivity is only 1/2 of the original. It is noteworthy that the situation is exceptional when the spinning amount is 4 mL. Due to the thickness of the lignin fiber membrane on the surface of the carbon paper, local shrinkage, aggregation and melting occurred during the carbonization process. This resulted in an uneven surface of the sample spinning at 4 mL and a large area without CNF coverage. This gives it a better air permeability and a worse electrical conductivity when measured. It is observed that the carbon paper sample prepared by ICAP has a large loss of CNFs, and the nanofibers cannot be completely embedded in the carbon paper and will drop during transfer or friction. This is also most likely the reason why the air permeability and resistivity of the 1 mL spinning sample are very similar to the blank control.

3.3. Carbon paper performance made by process IAPIC

Due to the large loss of ICAP prepared carbon paper [29], the process is further optimized. Adding an impregnated thermal pressure enables the lignin-based nanofibers to bind more closely with the carbon paper with the immersion process after the carbonization. Through two phenol resin maceration, as shown in Fig. 4, the overall tensile strength of the carbon paper sample was better than ICAP, reaching about 9 mPa. At the same time, the bending strength of the carbon paper sample has decreased significantly, and the whole sample is about 350 mPa [30, 31].
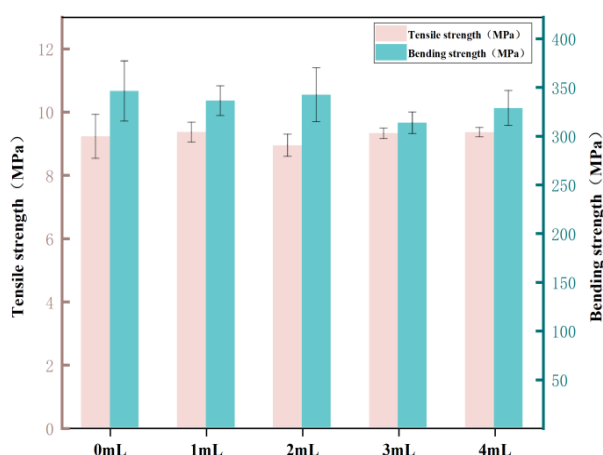
Fig. 4. Mechanical properties of carbon paper with different spinning amounts produced by process IAPIC.
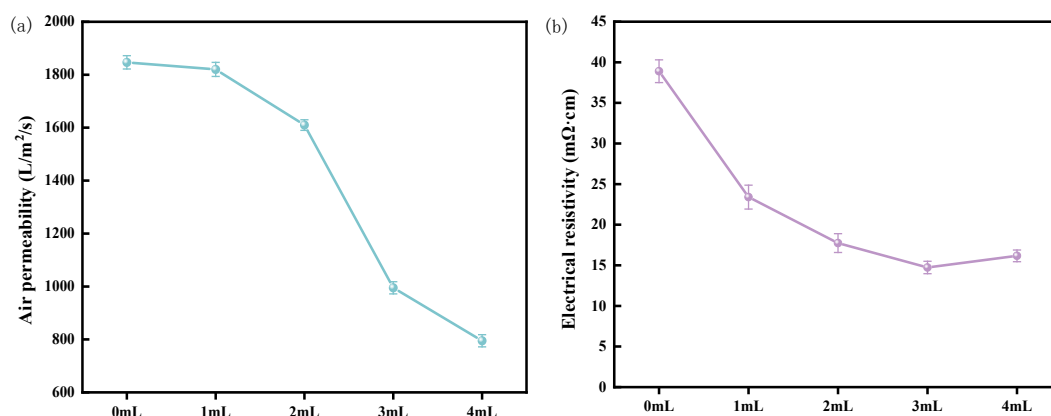

Fig. 5. Air permeability and electrical conductivity of carbon paper
with different spinning amounts produced by process IAPIC.

As shown in Fig. 5, the two imps had little influence on the air permeability of the carbon paper samples, with only a difference of about 100 L/m²/s. However, the loss of CNFs was greatly reduced, resulting in more pores being filled in carbon paper, so the permeability of carbon paper was significantly reduced with the increase of the spinning amount. When the spinning amount increased to 3 mL and 4 mL, the permeability was only 1/2 of that of the blank control group. The resistivity of the carbon paper sample decreases with the spinning amount until the spinning volume is 4 mL. Similar to ICAP, when the spinning amount reaches 4 mL, the too thick lignin-based nanofiber film will shrink and gather during carbonization, and the aggregated part will melt. This phenomenon makes the CNF filling less effective or even worse than before. When the spinning amount is 2 mL and 3 mL, the resistivity of carbon paper samples has reached a low value, but it also reflects the insufficiency of IAPIC: the uneven distribution of CNF. This phenomenon results in a very significant improvement in the sample resistivity sometimes from the blank control group.

3.4. Internal addition of CNF to carbon paper

3.4.1. Microscopic morphology

As can be found from Figure 6, the CNFs of the carbon paper prepared by this method can be kept between the carbon fibers, but after thermal pressure and the second carbonization, it is difficult to maintain the fiber structure. However, it can still regulate the pore structure of carbon fiber, establish connections, expand the conductive pathway, and thus enhance the conductive performance of carbon paper.
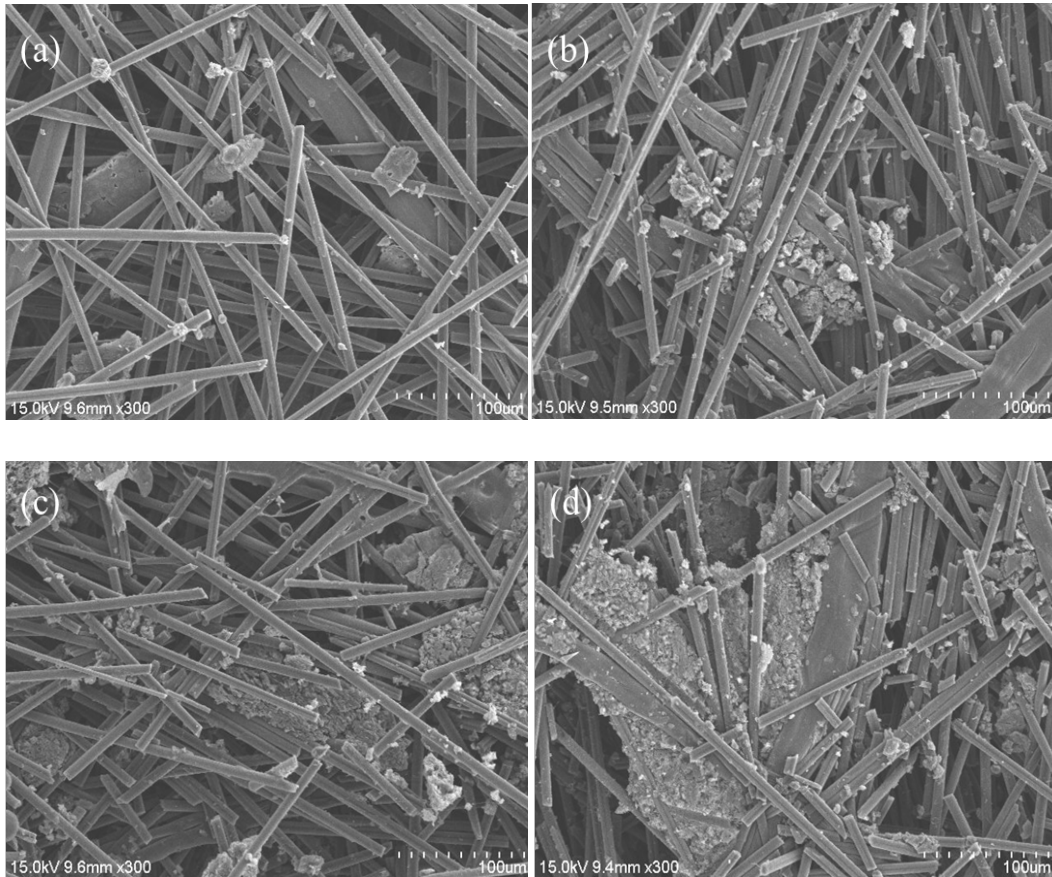

Fig. 6. SEM image of carbon paper with different CNF fillings: (a) 5 wt% (b) 10 wt%
(c) 15 wt% (d) 20 wt%.

3.4.2. Mechanical strength

In order to solve the problem of uneven distribution of CNFs in carbon paper, wet paper copying is used to add CNFs in the process of relieving carbon fibers and polyvinyl alcohol, so that the three are fully mixed evenly. The results showed that in this way, the CNFs were evenly distributed in the carbon paper samples. As shown in Figure 7, the air permeability decreases with the increase of filling amount, which is a predictable change. There is no obvious correlation with the amount of filling. Among them, with the increase of CNF filling from 0% to 15%, the tensile strength is slightly increased, which may be because under the combined action of CNF and phenolic resin, the original uncrosslinked carbon fiber has increased the strength.
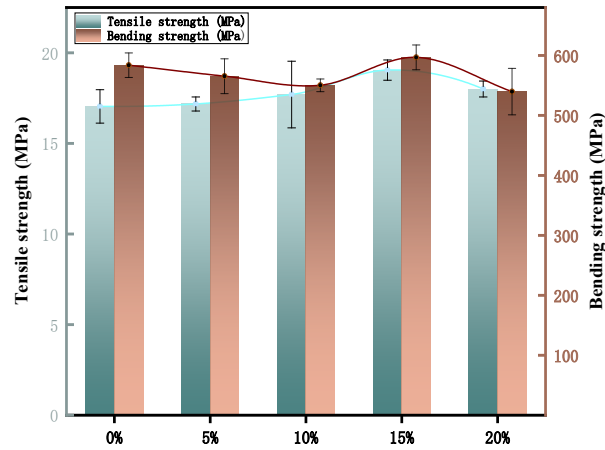
Fig. 7. Mechanical properties of carbon paper with different loadings of CNFs before carbonization.
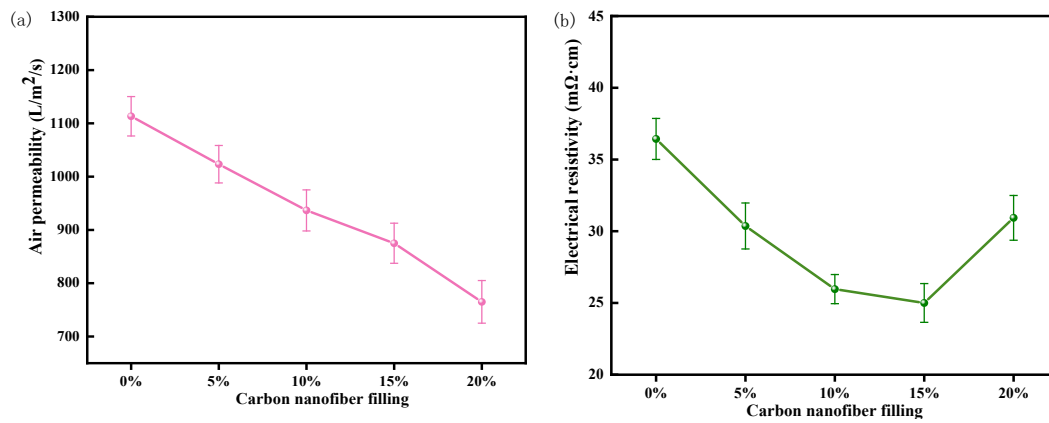

*Fig. 8. Under different CNF loading amounts, the air permeability and conductivity
of the carbon paper before carbonization.*

As shown in Fig. 8, the resistivity also decreases significantly with the increase of the filling amount in this range, and the resistivity error measured at different positions is small, which also proves that the addition of CNFs in the redistribution process can effectively solve the problem of uneven distribution in the ICAP and IAPIC. When the filling volume was increased to 20%, the tensile strength and electrical conductivity gradually deteriorated. This may be because when the filling amount is too much, the original connection mode of carbon fibers and CNFs becomes the connection between CNFs locally in the sample, so that the structure is not tight enough, which also affects the current transmission.
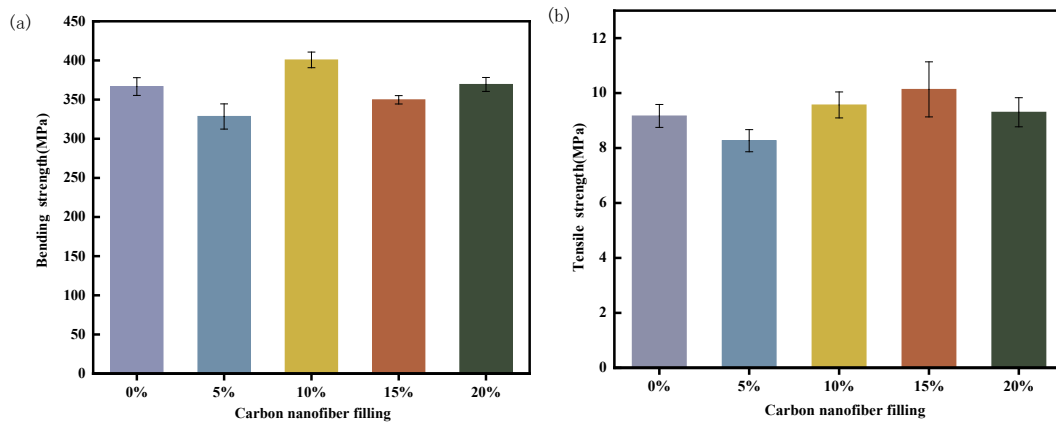
Fig. 9. For different CNFs Mechanical properties of carbon paper after carbonization.

In Fig. 9, the tensile strength of the sample after carbonization decreases from about 600 mPa to about 375 mPa. Meanwhile, the bending strength was reduced from about 17 mPa to about 9 mPa. The tensile strength is significantly reduced, because the bonding effect of the phenolic resin is reduced after carbonization, and under the action of high temperature, the phenolic resin becomes brittle, so that the bending strength is also affected.
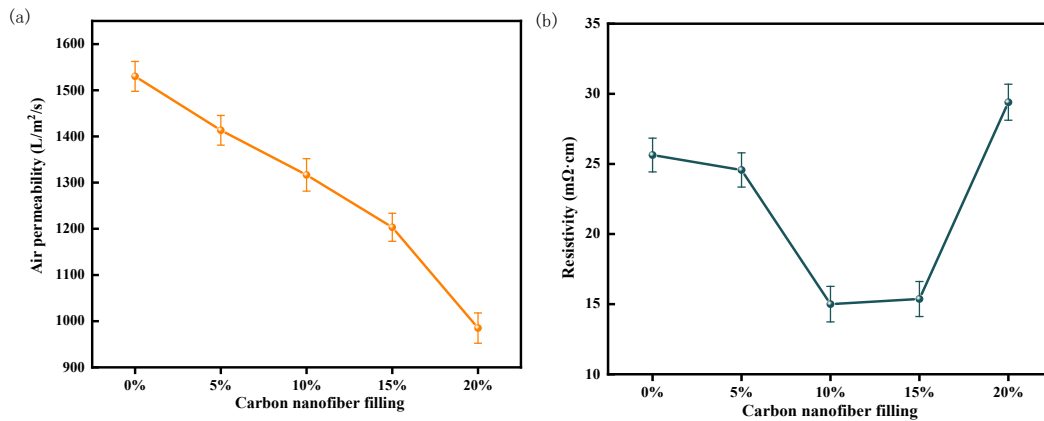

Fig. 10. With different filling amounts of CNFs Air permeability and electrical conductivity after carbonization of carbon paper.

From Fig. 10, the air permeability of the sample is significantly improved after carbonization, and the average value is increased from about 1000 L/m²/s before carbonization to 1300 L/m²/s. However, the resistivity was the lowest when the filling amount of CNF was 10% to 15%, and it was stable at about 16 mΩ.cm. Therefore, considering all the properties, when the filling amount of CNF is 10 wt%, the performance of carbon paper is improved best, and only less air permeability is lost, which almost does not affect the mechanical properties of carbon paper and significantly enhances its conductive performance.

4. Conclusions

This study explores four methods of directly incorporating lignin-based CNFs into carbon paper to regulate the internal pore structure of the carbon paper, thereby improving its physical strength, air permeability, and conductivity. Among them, the wet papermaking method can better disperse lignin CNFs in carbon paper, with the best overall performance. When the loading amount of lignin-based carbon fibers is 10%, the tensile strength is 9.4 mPa, the bending strength is 390 mPa, the air permeability is 1320 L/m^2/s, and the resistivity is 15 mΩ/cm.

Acknowledgments

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