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Ultra-thin carbon-fiber paper fabrication and carbon-fiber distribution homogeneity evaluation method

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Abstract. A preparation technology of ultra-thin Carbon-fiber paper is reported. Carbon fiber distribution homogeneity has a great influence on the properties of ultra-thin Carbon-fiber paper. In this paper, a self-developed homogeneity analysis system is introduced to assist users to evaluate the distribution homogeneity of Carbon fiber among two or more two-value images of carbon-fiber paper. A relative-uniformity factor W/H is introduced. The experimental results show that the smaller the W/H factor, the higher uniformity of the distribution of Carbon fiber is. The new uniformity-evaluation method provides a practical and reliable tool for analyzing homogeneity of materials.

1. Introduction

Carbon-fiber paper has been recognized as a primary material for MEA preparation of fuel cell due to its many attractive characteristics, such as high gas-permeability, high conductivity, high corrosion resistance and low density etc. As an extension material of Carbon fiber, carbon-fiber paper has also been applied for making super capacitor, lithium battery sandwich, electromagnetic shielding materials, aerospace materials, heating materials, functional materials, etc [1-6].

Many properties of carbon-fiber paper are strongly related with the thickness of carbon-fiber paper and plane-distribution uniformity, especially for the applications in fuel cell [7]. The distribution uniformity of Carbon fiber directly or indirectly affects the application of carbon-fiber paper [8]. For ultra-thin carbon-fiber paper, the distribution uniformity will play even more important role.

The preparation methods of carbon-fiber paper are mainly classified as dry-method and wet-method. Air-forming technique is generally used in dry-method preparation of carbon-fiber paper [9, 10]. In this technique, Carbon fiber are randomly overlapped each other to form a carbon-fiber net with uniformly thickness. Due to the electrostatic effect and many other characteristics, Carbon fiber are often mutual entanglement which results in an uneven-distribution. Therefore, the dry-method preparation of carbon-fiber paper is not yet widely applied. Wet-method paper-making is the main method at present to produce high quality carbon-fiber paper. The fabrication process mainly contents short cut Carbon fiber, fiber impregnated resin, dissociation, drying, hot pressing, high temperature carbonization and graphitization [11, 12]. The fabrication process of ultra-thin carbon-fiber paper has not reported yet.

Some research groups have reported their research work on the uniformity of fibers in carbon-fiber paper, but mainly in the initial stage. Hu [13] has reported the influence of dispersant on the dispersion

of Carbon fiber and paper evenness through analysis on the absorbent, resistance and tensile strength of carbon-fiber paper. The results obtained from the three methods are merely the same.

Su [14] reported that by using computer technology, the information of the vertical and the horizontal arrangement of Carbon fiber in the plane was obtained and analyzed. The influence of fiber length and the distribution on the twine phenomenon and on the pore structure of carbon-fiber paper has been studied. The results show that the large variation of Carbon fiber arrangement between vertical and horizontal direction in the carbon-fiber paper will reduce the uniformity of porosity distribution. Pan [15] reported fiber uniformity evaluation method for nano-fiber non-wovens based on time-frequency transform technology. Song [16] has also reported on uniformity evaluation method based on luminance uniformity of LED display screen. By obtaining the brightness information of CCD image through sensors, LED pixels are analyzed statistically, with the size of the standard deviation, the uniformity of brightness is evaluated.

In this paper, we will report a fabrication process of ultra-thin carbon-fiber paper and introduce a carbon-fiber plane-distribution uniformity evaluation method.

2. Experimental

The ultra-thin carbon-fiber paper fabrication process is presented in figure 1.

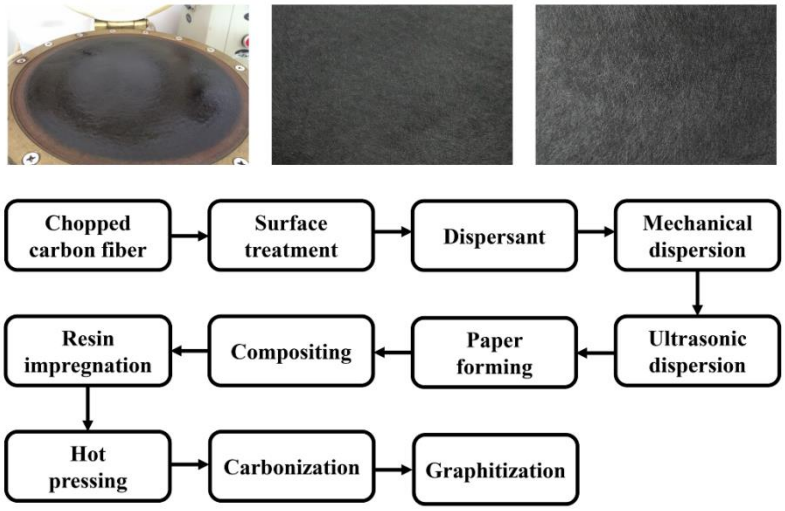

Figure 1. Schematic diagrams for preparation technology of ultra-thin carbon-fiber paper.

Firstly, Carbon fiber are cut to 6 mm long, and then, chopped fibers are put into a muffle furnace for a 90-minutes sintering at about 400℃. After sintering, the Carbon fiber are dispersed by using sodium carboxymethyl cellulose solution. Then, this carbon-fiber solution is put into ultrasonic cleaner for further disperse. After the ultrasonic treatment, the carbon-fiber solution is poured into a pattern forming device to form carbon-fiber paper blank. The carbon-fiber blank is then deposited on the filter and dry. The carbon-fiber paper blank is taken off from the filter by a positive-negative transfer method for further desiccation. The semi-finished carbon-fiber paper is then dipped into phenolic resin for completely impregnation. The naturally dried and impregnated semi-finished carbon-fiber paper will be hot pressed for 20 minutes at about 300℃. The pressure used in this process is 100 kg/cm^2. Finally, a carbonization process is carried out at 1450℃ for 3 hours in a vacuum furnace under high purity nitrogen gas atmosphere.

The gas permeability of the carbon-fiber paper is measured by YG-461E permeability tester and plane resistivity is measured by four-probe resistivity measurement method using WSP-22 four-probe resistivity tester.

The carbon-fiber distribution homogeneity is evaluated by a self-developed homogeneity analysis system based on average-pixel-filling statistics method. This system is based on the analysis of

filling/un-filling pixel point distribution for a two value picture. This homogeneity analysis technique is applicable to multi-fibers or similar materials those distributed randomly in a plane. With this system, an object picture is converted into a two-value picture first. The vertical and horizontal pixels of the picture are counted line by line. The ratio of filling to un-filling for each line is assigned to a variable "r". The number of lines those with equal ratio of filling to un-filling are accumulated and assigned to function "f(r)". For each f(r) - r curve, the half-height width "W" over the height "H" is defined as W/H. By comparing the W/H value of each sample, the plane-distribution homogeneity of ultra-thin carbon-fiber paper is evaluated.

3. Results and Discussions

3.1. Ultra-thin carbon-paper fabrications

The ultra-thin carbon-fiber paper before dipped in phenolic resin is shown in figure 2a and 2b. The density of Carbon fiber for this sample is 20 g/m^2 and the plane density of the sample is 0.0022 g/cm^2. The picture is taken in front of the computer screen. One can see that the sample is almost transparency due to its low plane density and ultra-thin structure. The gas permeability of this sample reaches 610 mm/s. A relatively low plane-density is obtained in comparing with commercial carbon-fiber paper such as Toray TPG-H-060. The plane density for TPG-H-060 is 0.0082 g/cm^2 which is about 3 times higher than present result. A little banding force (tensile 2.8 N) is tested which is attributed to the low plane-density.

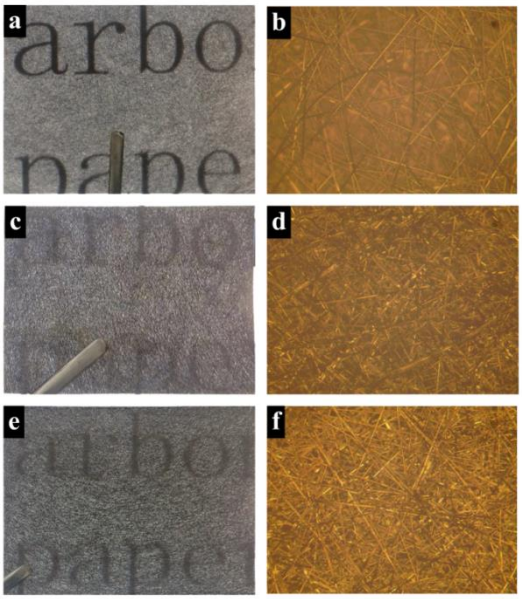

Figure 2. Conventional photos and optical images (40X) Carbon fiber paper at various pressing steps. a and b: before dipped in phenolic resin; c and d: after hot pressed; e and f: after 1450℃ and 3 hours carbonization.

With this semi-finished paper sample, an optical microscope photograph is shown in figure 2b. It shows that Carbon fiber are aligned randomly and no sodium-carboxymethyl-cellulose solution solidified substance and volatile residue exists around the crossing area of Carbon fiber. From figure 2b one can also see that the Carbon fiber are piled up randomly and almost no broken fibers. The region of blurred image indicates that the loose phenomenon of carbon-fiber superposition. This is because that no external pressure applied yet. Figure 2c presents a conventional photo of semi-finished carbon-fiber paper that took after dipped into phenolic resin and hot pressed. The effect of light transmission is obviously weakened due to the phenolic resin existence. Figure 2d shows the morphology of carbon-fiber paper after the hot pressed. Little solidified phenolic resin can be clearly seen in figure 2d. This may reduce the property of the carbon-fiber paper as it may cause a un-uniformity of surface density and the surface resistivity. From figure 2d one can also see that some broken Carbon fiber on the surface. This is directly related to the effect of hot pressing. Figure 2d

indicates that the pressure we used in hot-pressed procedure is acceptable. In this paper, about 100 kg/cm^2 pressure is applied and the thickness of the semi-finished carbon-fiber paper at this stage is 0.093 mm.

The phenolic resin existence induces a remarkable enhancement of the plan density (from 0.0022 g/cm^2 to 0.0040 g/cm^2) and the tensile (from 2.8 N to 12 N) comparing with the semi-finished carbon-fiber paper that before dipped into phenolic resin. In the meantime, decreasing of the plane resistance (from 160 mΩ•cm to 140 mΩ•cm) as well as the gas permeability from 610 mm/s to 330 mm/s are found. From figure 2d one can also see that due to the increasing of the density caused by hot pressing, the blurred phenomena that can be seen from figure 2b disappeared，the number of visible carbon-fiber increased significantly and the fluffy phenomena decreased. Figure 2e shows the conventional optical photo of carbon-fiber paper after 1450 ℃ carbonization. Comparing figure 2e to figure 2c, the light transmission effect is slightly difference. Relatively sharp characters show in figure 2e proofs that the influence of carbonization on the light transmission of the carbon-fiber paper is positive. The thickness of the carbon-fiber paper is also decreased due to the carbonization process (from 0.093 mm to 0.090 mm), while, the plane density and the plane resistivity decrease remarkably, that means the carbonization process cause the carbon-fiber paper shrink a little. This shrink is mainly related with the mass evaporation: almost 14% resin volatilized during the carbonization process. As results, the gas permeability of the carbon-fiber paper increases from 330 mm/s to 410 mm/s. Further higher gas permeability can be expected after higher temperature graphitization. Figure 2f shows morphology picture after carbonization. From figure 2f one can see that only a small portion of phenolic resin remains between Carbon fiber and porosity increased significantly. Tensile of the sample increases from 12 N (before carbonization) to 19N after carbonization which indicates that the Carbon fiber bond each other even tightly. From figure 2f one can find that the Carbon fiber are mostly remain their original length without broken. An enhanced porosity can be expected after graphitization treatment. The plane resistivity of the sample after the carbonization is equal to 30 mΩ•cm, much lower than one after the hot-pressed (140 mΩ•cm). However, it is still very high in comparison with Toray's TPG-H-060 which is about 5.8 mΩ•cm (graphitized). This is because the relatively low carbonization temperature we used in this paper.

Table 1. Some physical parameters for ultra-thin Carbon fiber paper with different states.

	Before dipped into phenolic resin	After hot pressed	After carbonization	Toray TPG-H-060
Plane density	0.0022 g/cm^2	0.0040 g/cm^2	0.0033 g/cm^2	0.0082 g/cm^2
Thickness	0.120 mm	0.093 mm	0.090 mm	0.185 mm
Plane resistivity	160 mΩ•cm	140 mΩ•cm	30 mΩ•cm	5.8 mΩ•cm
Tensile strength	2.8 N	12 N	19 N	34 N
Carbon fiber content	20 g/m^2	20 g/m^2	20 g/m^2	/
Permeability	610 mm/s	330 mm/s	410 mm/s	500 mm/s

Table 1 presents some parameters of ultra-thin carbon-fiber paper at different preparation states. The plane resistivity will be decreased and the tensile strength will be increased if graphitization finished.

3.2. Evaluation of Carbon fiber distribution homogeneity

One of important factors that affect the property of Carbon fiber paper is homogeneity of carbon-fiber distribution. In this paper, we introduce a self-developed homogeneity analysis system for evaluating carbon-fiber distribution uniformity of carbon-fiber paper.

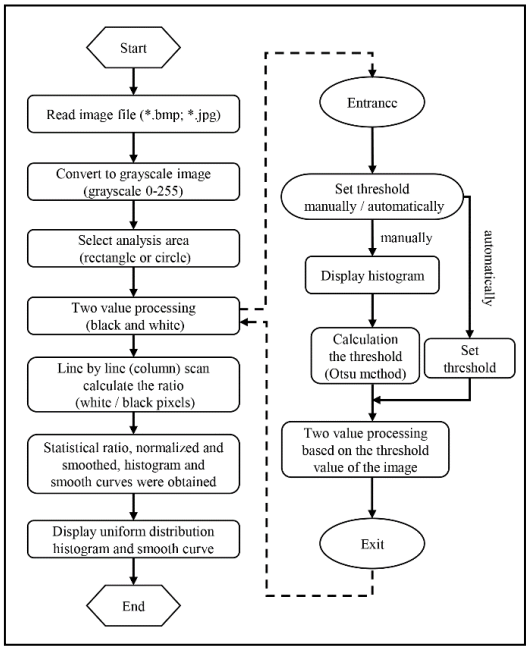

Figure 3. Flow charts of the self-developed homogeneity analysis system.

Figure 3 represents the flow chart of the analysis model used in the self-developed system. To evaluate the Carbon fiber distribution of one or several carbon-fiber paper samples, one can take images for each sample with the same magnification and size. The analysis program works as following: firstly, converting an image of object sample into a two-value image, then, the ratio of black and white pixel on each horizontal and vertical lines of the two-value image is calculated. The lines those with same ratio (r) are accumulated and labeled with f(r). A graph can then be drawn by taking f(r) as y-axis and (r) as x-axis. For a sample that the Carbon fiber are randomly distributed, this program will generate a single smoothly and regularly peak. This method is applicable only to analysis those images with multi fibers or particles and randomly plane distribution. There are some extreme cases, for example, un-randomly distributed situation; figure 4 presents the analysis results.

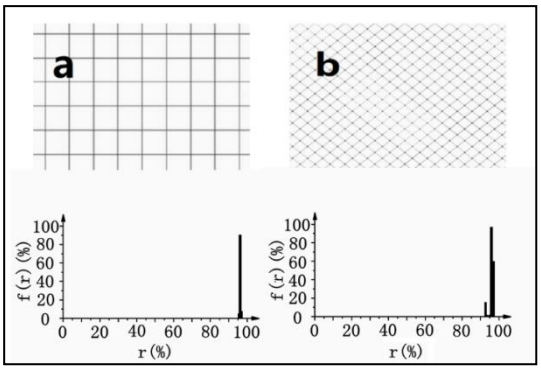

Figure 4. Distribution functions f(r) for two ideal uniformly (un-randomly) distributions of fiber material.

By applying this model, a graph with ideal uniformly (un-randomly) distribution of fiber material should be one or more straight line perpendicular to the horizontal axis. Figure 4a and 4b showed this case. Figure 4 represents the case that for a homogeneous distribution, there is only one or few ratio of filling pixel to un-filling pixel exist throughout the whole picture. The distribution function will be a few vertical lines only.

For an image with a randomly distribution structure, the homogeneity distribution is evaluated by the factor (W/H), while, W is the half height width of fitting curve f(r) and H is the peak height of fitting curve f(r). The better the distribution uniformity, the smaller the W/H value is.

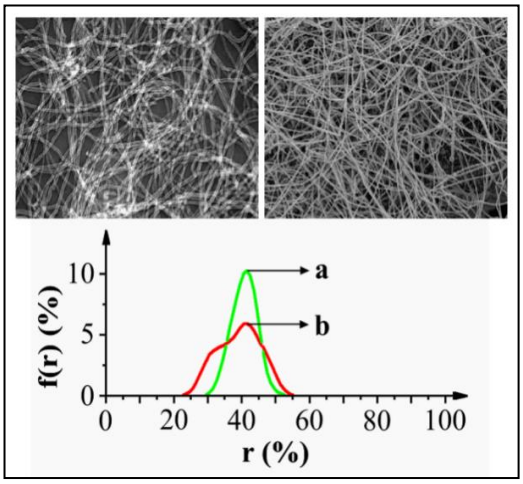

Figure 5. Distribution functions f(r) for two samples: curve "a" represents upper right-side image, curve "b" represents upper left-side image.

In figure 5, we chose two samples with different distribution uniformity remarkably that can be easily distinguished visually. By applying this analysis system to figure 5, we get two distribution curves. In figure 5, the curve "a" (W/H = 0.9) corresponds to the upper-right side picture which has better plane distribution than the upper-left side one. The left side picture is represented by the curve "b" (W/H = 3.1) in the figure 5. One can see that the distribution function f(r) is strongly related with the distribution homogeneous of the sample.

To applying this model to the homogeneous analysis on the ultra-thin carbon-fiber paper presented in this paper, we choose figure 2b, 2d, and 2f as analysis objects and study the relationship between the fiber distribution uniformity and the distribution function (curves) of these three images. The results are shown in figure 6. The curve "a" represents figure 2b, sample before dipped into phenolic resin. The curve "b" represents figure 2d, sample after hot-pressed and the curve "c" represents figure 2f, sample after carbonization; Table 2 shows the W/H values for each sample.

Table 2. W/H values for various samples.

Sample	Curve	W/H
Sample before dipped into phenolic resin	"a"	0.16
Sample after hot-pressed	"b"	0.23
Sample after carbonization	"c"	0.22

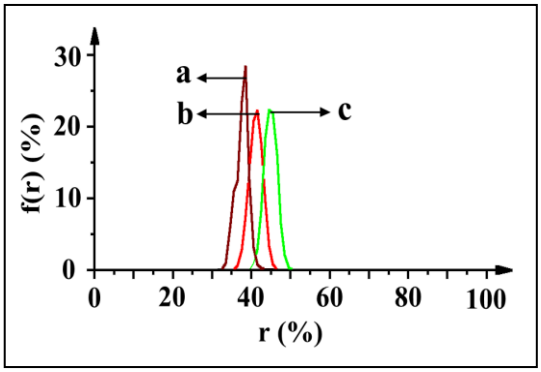

Figure 6. Distribution functions f(r) for three samples of carbon-fiber paper. Analysis is done based on figure 2b represented by curve "a", figure 2d represented by curve "b" and figure 2f represented by curve "c".

In figure 6, curve “a” shows a small different with curve “b” and “c”. This is because that there is no resin added at this stage. Foreign substance, in this case is resin, contribute negatively to the analysis result. Curve “b” and “c” are nearly the same indicating that the carbon-fiber distribution ie same at these two steps. This is understandable because that both these two samples are resin added, the hot-press and carbonization treatment hardly can influence the carbon-fiber distribution. Figure 6 implies that this analyst technique is applicable only under certain condition: objects’ image should be comparable.

4. Conclusions

Ultra-thin carbon-fiber paper (0.09 mm thickness) has been fabricated. The distribution uniformity of the Carbon fiber play a key role in identifies the quality and properties of ultra-thin carbon-fiber paper. By applying the self-developed distribution homogeneity analysis system introduced in this work, the homogeneity distribution of Carbon fiber in carbon-fiber paper has been analyzed. W/H can be used as a factor to evaluate the uniformity of randomly distributed carbon-fiber paper.

Acknowledgments

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