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Electrical Resistivity of Active Carbon Nonwovens

Abstract
The electrical properties of the grainy forms of active carbon are well known, but their use is limited by the small electrical contact which occurs between the grains. A growing interest in fibrous carbon materials can be observed, which is mirrored in the literature concerning electrode materials. Among other things, this results from the fact that they ensure good electron conduction along the fibres, as well as a nearly stable spatial fixing of the fibres throughout the whole carbon material. From the point of view of electrochemistry, fibrous carbons seem to be a distinctive and interesting group of active carbons. They are perceived as electrode materials for electrochemical capacitors, since one of the requirements for electrochemical capacitors is their low internal resistance. The effect of the technique and procedures for making a nonwoven fabric precursor on the magnitude of the electrical resistivity of active carbon nonwovens manufactured from this precursor has been studied within the investigation presented in this work.

Key words: *precursor nonwovens, active nonwovens, active carbons, carbon materials, electric resistivity.*

Introduction

A capacitor is an element of relatively small overall dimensions, used in electrical systems, designed for the accumulation of considerable electric charges. The simplest, plate capacitor is made up of two metal plates of equal dimensions, placed in parallel to each other and separated by a dielectric. When voltage from a direct current source is applied to the plates, an electrical charge is accumulated on them. Considering the structure and the principle of the operation, we can classify capacitors as electrical, electrolytic and electrochemical.

An electrochemical capacitor consists of two stationary electrodes divided by a separator whose function is to separate the electrodes from the electrolyte. The electrochemical capacitor's operation consists in accumulating an electric charge at the electron conductor- ion conductor phase boundary, where no electrochemical reactions occur. The advantages of this type of capacitor include the high speed of electric charge propagation, the absence of chemical reactions in the electrode materials and hence a long working life, and finally an ecologically-safe construction. They are used in systems which require high-density power supply of short duration, e.g. as in electrical vehicles (where the need arises during start-up, acceleration and while driving uphill), in pulse and laser technologies, emergency power backup systems (UPS in computers for providing power during a mains power failure), integrating elements in low-voltage electric circuits, and for interaction with solar batteries to increase their power.

The magnitude of an electric charge accumulated by an electrochemical capacitor depends, among other things, on the electrode material and the composition of an electrolyte solution. Analogous processes as in a conventional metal-electrolyte system occur at the active carbon-electrolyte phase boundary.

Carbons of different forms are widely used in electrochemistry. This is because they meet the conditions imposed on electrode materials, i.e. they are capable of accumulating an electric charge, have good electrical and thermal conductance, a large inner area, and show considerable resistance against the aggressive action of electrolytes [1]. From the point of view of electrochemistry, fibrous carbons alone seem to form an interesting and distinctive group of active carbons. Compared with grains and granulates, active fibrous carbons are characterised, among other things, by a partially ordered structure, which ensures good electron conductance along the fibres, and a nearly stationary spatial fixing of the fibres in the product, which ensures good contact between them.

As mentioned above, one of the requirements of electrochemical capacitors is low internal resistance, which results from the resistance of the electrode material used. This depends on a number of factors. Among the most important are the type of fibres and the degree of their internal structure, which are mainly related to the treatment temperature during processing, the thickness of fibres and the development of their edge line, the arrangement of fibres in the nonwoven, and the number of electrical contacts between them. In this case, the fibres' resistance results from the conductance properties of the fibre and the nonwoven structure.

An increase in interest in the electrical properties of fibres has been observed in the last few years. Evidence for this interest is the information which has been appearing in publications connected with this problem. For example, Delacroix et al. [3] have noted that with the increase in the carbonisation temperature of viscose woven fabrics within the range of 600-900°C, the electrical resistance of these fabrics decrease to a value of a few ohms, and next becomes stabilised

upon a further temperature increase. Grint et al. [4] investigated the electric resistance of active carbon woven fabrics manufactured from a viscose precursor. Grint obtained different distributions of meso- and micro-pores in active carbon by means of applying various parameters of thermal processing. The electrical resistance of the active carbon woven fabrics which he tested came to over twenty ohms. Tanahashi et al. [5] determined the electrical resistance of materials formed by the papermaking technique designated for electrodes of double electric layer capacitors. This nonwoven material consisted of 65% carbon fibres obtained from pitch, 20% active carbon fibres manufactured on the basis of the Kynol precursor, and 15% binding agent in the form of a polyethylene dispersion of natural fibres. The electrical resistance of this composition equalled 18 ohms. Zhong et al. [6] tested two types of commonly manufactured electrode materials most often used in electric cells. These materials were manufactured as graphite felts based on a polyacrylonitrile precursor and on artificial rayon (viscose filament fibres). The authors stated that the electrical conductivity of graphite felts manufactured from PAN precursors is better than those achieved for the rayon precursor, notwithstanding the fact that both felts have a similar structure.

The Aim of Investigation and Assumption Accepted

The aim of this investigation was to estimate whether, and if so to what degree, it is possible to influence the resistivity of active carbon nonwovens which are predestined as electrode material in electrochemical capacitors, at the stage of nonwovens precursor manufacturing. However, this manufacture should be done on condition that the parameters of further processing are optimised to achieve maximum porosity of the fibres.

The investigation carried out was based on the approach of applying nonwoven techniques for manufacturing precursor nonwovens with parameters which could ensure the obtention of active carbon nonwovens (after the processes of carbonisation and activation) characterised by features which would meet the requirements for electrode materials.

Viscose fibres were selected as raw material for the precursor nonwovens. These fibres are characterised by a highly developed internal surface and a certain fibre's porosity. These features are advantageous for carbon precursors designated as intermediate products for electrode material [7].

The elaboration of the procedure for manufacturing precursor nonwovens was aimed at obtaining a structure which would ensure the following assumptions:
- as many fibres as possible should be in the position perpendicular to the surface,
- as many contact points as possible between the particular fibres should be formed, and
- the specific mass of the precursor nonwoven should be as great as possible for the assumed thickness.

It was assumed that the realisation of the two first points would decrease the nonwoven's volume resistance and facilitate the free flow of electric charges. The low internal resistance of the electrode material is one of the basic requirements for the construction of electrochemical capacitors.

Experimental Part

The precursor nonwovens were manufactured from viscose raw materials whose parameters are presented in Table 1. The webs (all from viscose raw materials) were prepared by two methods, dry-laying and wet-laying.

From the webs prepared, the following were obtained:
- needled nonwovens (by applying changeable technological parameters);
- needled and adhesive threaded nonwovens, by introducing a liquid binding agent in the form of an aqueous dispersion of a phenol resin from the resol group. The binding agent was applied by means of a spray, deposition and padding, and its content differed in the particular nonwovens;
- some of the nonwovens obtained were finished by means of pressing with the use of calendering cylinders;
- nonwovens manufactured by means of the papermaking technique. Phenol resin of the resol type, acidified by HCl to pH 4, was used as the binding agent. The nonwovens were formed in some variants which differed from each other by the kind of grinding (in the dry or the wet state), by the various fractions of fibre lengths applied, and by the different masses of the fibres;
- hydro-entangled nonwoven (nonwovens manufactured in Lentex S.A.).

The precursor nonwovens obtained according to the methods mentioned above were carbonised and activated with the aim of obtaining carbon and active nonwovens. The carbonisation process of the precursor nonwovens was conducted in a medium of steam and gases, which were liberated from the fibres at a temperature of up to 600°C. Thermal processing was carried out by means of the periodic method in a chamber reactor at a temperature which was slowly increased. The carbon nonwovens were activated at the second stage of the technological process by means of the physico-chemical method, with the use of a water steam as activator, and at a temperature of 850°C.

The following estimation criteria were accepted for the precursor-, carbon-, and active-nonwovens obtained:
- the value of through resistivity,
- the result of an organoleptic estimation.

The tests of the nonwovens through resistance have been performed perpendicular to the nonwoven's surface. To secure these conditions, a system of circular electrodes was used, with the tested sample placed between them. The resistance tests were carried out in accordance with standard PN-EN 1149-2 [9] at a relative air humidity of 30%, and an air temperature of 23°C.

The resulting resistance was indicated by an IM-6 Radiometer megaohmmeter at the range of 20 Ω with accuracy of ±5%, and an MX53-4650 digital multimeter at the range of 200 Ω with accuracy ±1%.

Table 1. *Parameters of viscose fibres.*

Type of fibres	Linear density, dtex	Length, mm	Resistance, Ω
Viscose	4.4	70	8.27×10^8

The resistivity of nonwovens was calculated from the following equation:

$$R = Rw \times S / d$$

where:
R - resistivity, in Ωm,
Rw - through resistance, in Ω
S - surface of the electrode, in m^2, and
d - thickness of the nonwoven sample, in m.

The organoleptic estimation was carried out considering the nonwoven's arrangement ability and its surface uniformity. Rigid samples and samples with an irregular surface were eliminated. The results obtained are presented in Tables 2-4.

Analysis of the Results

The technological manufacturing parameters for the individual variants of the selected precursor nonwovens are presented in Table 2, together with their morphological characteristics. The following nonwovens were selected: needled, needled and adhesive threaded, calendered, wet-laid nonwoven (formed by the papermaking technique), and hydroentangled nonwoven. The results which considered the variants of the adhesive threated nonwovens which were manufactured by deposition or padding of the binding agent are not presented, because these nonwovens had already been organoleptically estimated as bad at the stage of manufacturing the carbon nonwovens. They were very rigid, and at the same time fragile and brittle. These features eliminated the possibility of application as electrode material, independent of the estimation of other parameters assessed. An analysis of the results listed in Table 2 allows us to state that the highest specific mass among precursor nonwovens was achieved for the calendered nonwovens (variant 3), whereas the lowest came for nonwovens formed from an isothropic web (variants 1 and 5). Among the active nonwovens, the highest specific mass have the nonwovens obtained by means of variants 3 and 5, whereas the lowest was found in those obtained by variants 1 and 4 (see Table 3). The values of apparent density of the active nonwovens manufactured by the individual variants are graphically presented in Figure 2.

Table 2. *Characteristic of precursor nonwovens.*

Variant number	Manufacturing technique	Surface mass, g/m²	Thickness, mm	Apparent density, g/cm³
1	Dry-laying, random laying, needled	470	3.31	0.1420
2	Dry-laying ,parallel laying, needled	679	3.83	0.1772
3	Dry-laying, parallel laying, needled, calendered	814	1.69	0.4827
4	Dry-laying ,parallel laying, needled, spraying 1% of resin	686	3.84	0.1750
5	Dry-laying, random laying, needled, spraying 8% of resin	1056	6.95	0.1468
6	Dry-laying, parallel laying, needled, spraying 20% of resin	976	6.30	0.1549
7	Wet-laying, , random laying dry grinding, 15% of resin	353	1.67	0.2116
8	Wet-laying, random laying , dry grinding, 15% of resin	238	1.25	0.1907
9	Wet-laying, random laying , wet grinding, 15% of resin	190	0.91	0.2085
10	Wet-laying, random laying , wet grinding, 20% of resin	227	2.25	0.1080
11	Dry-laying, random laying, hydroentangled	73	0.60	0.121

Table 3. *Characteristic of active nonwovens.*

Variant number	Surface mass, g/m²	Thickness, mm	Apparent density, g/cm³	Organoleptic estimation
1	122	2.42	0.0505	very good
2	228	3.51	0.0644	very good
3	271	2.35	0.1152	good
4	192	3.47	0.0554	very good
5	224	2.35	0.1251	good
6	213	3.31	0.0644	sufficient
7	160	1.69	0.0973	sufficient
8	92	1.40	0.0654	good
9	66	0.92	0.0920	good
10	90	0,88	0.1017	good
11	57	0.56	0.1020	very good

Table 4. *Through resistivity of precursor nonwovens obtained according to the various variants and of the active nonwovens obtained from them.*

Variant number	Through resistivity of nonwovens	
	Precursor, Ωm x 10^8	Active nonwoven, Ωm
1	3.88	1.10
2	1.92	1.34
3	4.33	1.54
4	1.24	0.27
5	3.00	0.54
6	1.60	1.04
7	9.90	0.92
8	18.8	1,02
9	14.2	1.17
10	15.7	1.25
11	107.0	0.98

Table 4 shows the measurement results of electric resistivity, obtained for the tested precursor and active nonwovens. As can be seen from the presented results, the resistivity values of active nonwovens decreased by eight orders compared with the values of precursor nonwoven resistivity. The influence of the manufacturing techniques for the precursor nonwovens on the resistivity value of the active nonwovens obtained from them are graphically presented in Figure 1. It is clearly visible that active nonwovens obtained from the precursor manufactured by the needling technique with a small amount of resin introduced into the processed material (variants 4 and 5) are characterised by the lowest resistivity.

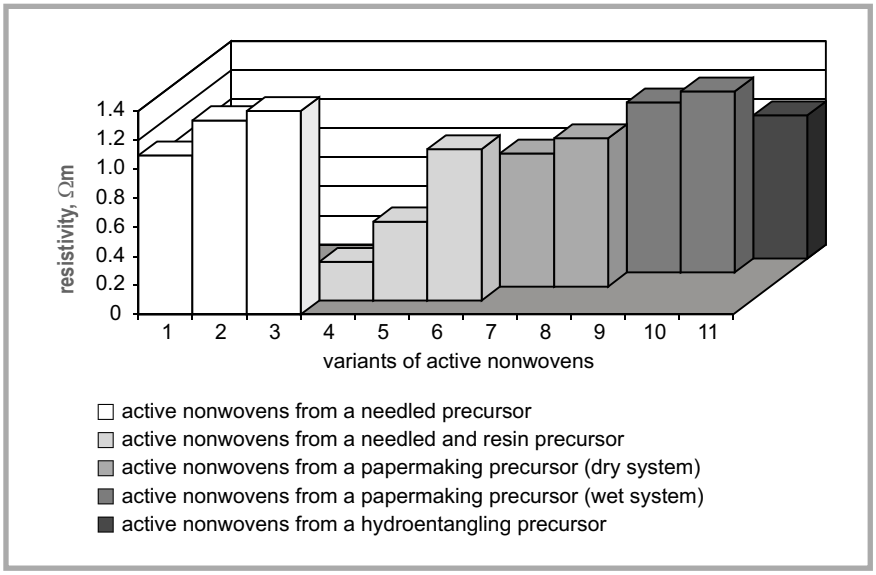

Figure 1. *Resistivity of active nonwovens.*

The resistivity of the collection of conductive fibres, which in reality is an active nonwoven, depends on two factors. The first is the carbon structure of the individual fibres, especially the order of the arrangement of the fibres' conductive surface layers. The second factor is the number and quality of the electric connections between the fibres forming the nonwoven. For the investigated nonwovens, the thermal processing during activation was performed for all fibres at the same temperature. From this, it results that the degree of internal reconstruction and structure arranging were the same. Thus, the effect of the different mutual fibre connections must be the reason for the diversification of resistivity. It seems that an isotropic arrangement of fibres creates a more advantageous effect of lowering the through resistivity compared with an orthotropic arrangement (obtained after processing with the use of a carding machine), and this nevertheless causes the lower fibre concentration. On the other hand, an increase in fibre concentration (in the specific mass of the nonwoven) caused by calendering (as in variant 3) does not cause the assumed decrease in resistivity. This may lead to the conclusion that a significant increase in the number of contact points between the fibres did not take place, nor did any improvement in its quality (which further means that the contact areas have small resistivity).

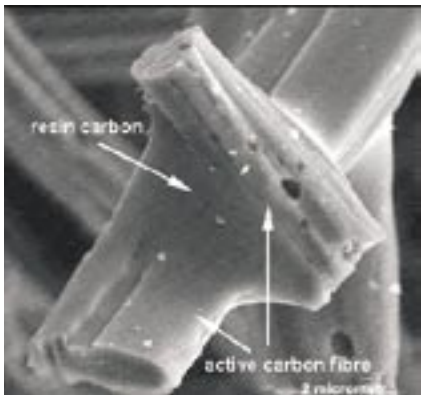

Figure 2. *SEM photography of a nonwoven prepared from viscose fibres with a small amount of phenol resin deposited on its surface (below 5% of mass), then pyrolised and activated at a temperature of 850°C.*

The resistance of fibres coated by a layer of phenol resin behaves quite differently. In this case, independent of the nonwoven manufacturing method and its density (Figure 2, variants 4-6), the resistivity depends mainly on the amount of the resin introduced alone, and what is more, inversely proportional to this amount. Fibres coated by the smallest resin amount have the smallest resistivity, and when the content of the latter in the fibre mass increases, its resistivity also increases. The carbon matrix of fibres obtained from viscose is composed from a significant number of arranged fragments which form graphen layers [8] with very good electrical conductivity. In contrary, the fibres coated by an amorphic carbon layer which originated in the phenol resin processed at the same temperature (850°C) are less conductive and have higher resistivity. From the abovementioned, the conclusion can be drawn that coating the surface with thicker and thicker layers leads to an increase in the resulting resistivity of composite fibres. However, this group of active nonwovens is characterised by the lowest resistivity among all nonwovens investigated. It should be expected that the resin has advantageously influenced the lowering of the electric connections between the fibres, thanks to the mutual gluing of the individual fibres of viscose origin. This means that further the electric current path in the nonwoven consists only of the viscose fibres' surface, and the resin only joint durable the fibres (at 1% of resin), in contrary to the case where with a greater resin amount (8% or more), an additional isolating layer is formed.

Figure 2 shows fragments of viscose fibres coated by a phenol resin, then pyrolised and activated. The carbon residue of the resin glues two mutual contacting fibres, and as can be assumed, significantly improves the electric conduction between these fibres, while at the same lowering the nonwoven's resistivity. The small amount of resin which pour-wetted the fibres was mostly deposited at the fibres' crossing. These observations prove the truth of the above mentioned considerations.

The results of the organoleptic estimation of the active carbon nonwovens are presented in Table 3. Of all the processing variants of the carbon nonwovens tested, the best organoleptic evaluation was achieved by the nonwovens manufactured from the nonwoven precursors which were needled classically (variant 1 and 2), the nonwovens needled with addition of resin (variant 4), and the nonwovens obtained by variant 11, i.e. from the precursor needled by means of water.

The nonwovens of variant 5 are characterised by a worse organoleptic estimation, which results from its rigidity. The active nonwovens obtained on the basis of the nonwovens manufactured by the papermaking technique are in general characterised by greater rigidity and fragility, similar to the active nonwovens obtained on the basis of needled and calendered nonwovens, and for nonwovens needled by means of water (variant 11).

Considering both the most important criteria of active nonwoven's estimation, i.e. through resistivity and organoleptic estimation, we can state that the best results were achieved for needled nonwovens containing 1% of binding agent (variant 4), and for nonwovens needled by water (variant 11).

Conclusions

The values of resistivity of the active carbon nonwovens can be established by selecting the nonwoven precursor processing technique.

Considering the values of electric resistivity obtained, and the organoleptic estimation, the best active carbon nonwoven was obtained from the following precursors:

- manufactured by the needling technique (the active nonwoven's resistivity obtained equalled 0.27 Ωm);
- needled by means of water (the active nonwoven's resistivity obtained equalled 0.98 Ωm); and
- needled classically technique (the active nonwoven's resistivity obtained equalled 1.09 Ωm).

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