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Resistance of Carbon and Active Carbon Precursor Nonwovens

Abstract

Active carbon nonwovens tend to be attractive intermediate products for electrochemical sources of electric current; they may be applied as electrode material in electrical capacitors and super-capacitors. Low internal electrical resistance of the electrode material is an indispensable condition for manufacturing good capacitors. This article presents the results of investigations we have carried out into developing active carbon nonwovens from regenerated cellulose. Three types of cellulose were used, and the influence of the precursor type on the resistance of the active carbon nonwovens was estimated. Only a small dependence of the kind of precursor used on the nonwoven's resistance was stated. The resistance values achieved (of the through resistance below 1 ohm and of the surface resistance about 1 ohm) allow us to state that these parameters fulfil the conditions for electrode materials of electrochemical capacitors.

Key words: electrode materials, resistance, active nonwovens.

Introduction

Electrochemical capacitors are used for the accumulation of electric energy stored in the form of electric charges on the phase boundary of the electron and ion conductors. An electrochemical capacitor consists of two solid electrodes placed in an electrolyte solution and separated by a microporous ion-permeable separators. The ability to achieve periodical durability and high capacities and high power at discharging arises from the working principle of the electrochemical capacitors, i.e. storing electric charges without proceeding electrochemical reactions [1]. An indispensable condition for high power consumption is low electric resistance of the system resulting in the use of electrode materials with as low a resistance as possible. Active carbon materials are very attractive among materials which permit high electric capacity to be obtained. These are characterised by considerable structure orientation when compared to pulverised carbon, grains, and granules. This feature allows us to achieve good electronic conductance along the fibres and almost stable three-dimensional fixing of the fibres which ensures good contact between them. Such carbons are manufactured by means of thermal and oxidation processing of fibrous materials, among which regenerated cellulose fibres appear to be very attractive. This results from the abi-

lity to achieve high parameters of the porous structure and of the surface's chemical structure. The pyrolysis of various cellulose fibres takes place at a temperature of about $320 \pm 15^\circ\text{C}$, and leads to the destruction of the cellulose chain, to the breaking of the oxygen bridges and to the disintegration of glycoside rings. The conducting structures appear newly formed in the carbon matrix at a temperature of above 380°C . The carbon remains of the glycoside rings begin to form six-segmental aromatic rings which, upon further increase in temperature, join together into larger and larger condensed fragments in the shape of graphen layers of low resistivity. Such a structure confirms the approach of applying carbon fibres in electrochemical capacitors. In general, the technological parameters of manufacturing active carbon nonwovens have been optimised with the aim of achieving a large surface of the pores and a 'rich' chemical structure of the surface; both these features influence the charge amount stored on the electric double-layer of the capacitor.

The capacity loss of the capacitor to a considerable degree results in its resistance, which in turn is the result of the conductive features of fibres and the nonwoven's structure. The following factors influence the nonwovens' resistivity: the kind of fibres, the degree of their internal arrangement (connected mainly with the temperature of processing), the thickness of the fibres, the development of their surface, the way in which the fibres are positioned in the nonwoven, and the number of contact points between the fibres.

The aim of this investigation was to estimate whether and to what degree it is possible to influence the resistance of active

carbon nonwovens predestined as electrode material in electrochemical capacitors at the stage of cellulose precursor selection, under the condition that the parameters of further processing have been optimised to achieve the maximum porosity of the fibres.

Experimental

For these investigations, three types of regenerated-cellulose fibres produced by the Austrian company Lenzing were selected. The fibres are made using different technologies, and so differ from one another in both their physical properties and structure [2]. The characteristics of the fibres are presented in Table 1.

The procedure for manufacturing precursor nonwovens was elaborated with the aim of obtaining a structure which would meet the following requirements:

- as many fibres as possible should be in the position perpendicular to the surface;
- as many contact points as possible should be formed between the particular fibres, and
- the specific mass of the precursor nonwoven should be as great as possible for the thickness assumed.

Table 1. Characteristics of the precursor fibres.

Variant	Type of fibres	Linear mass dtex	Length mm
I	Lenzing Modal	3.3	40
II	Lenzing Modal	1.7	40
III	Lenzing Lyocell	3.3	40
IV	Lenzing Lyocell	1.7	40
V	Lenzing Viscose	1.7	40

Table 2. Characteristics of the carbon and active precursor nonwovens.

Variant number	Type of fibres	Precursor nonwovens					Carbon nonwovens					Active nonwovens				
		Surface mass		Thickness		Apparent density	Surface mass		Thickness		Apparent density	Surface mass		Thickness		Apparent density
		m _p	V	l	V		m _p	V	l	V		m _p	V	l	V	
		g/m ²	%	mm	%	g/cm ³	g/m ²	%	mm	%	g/cm ³	g/m ²	%	mm	%	g/cm ³
I	Lenzing Modal 3.3	728.9	7.4	7.20	6.7	0.091	302.3	8.3	4.85	7.1	0.062	191.4	9.2	4.22	11.5	0.045
II	Lenzing Modal 1.7	602.5	9.0	6.62	10.1	0.104	292.4	9.7	4.64	10.3	0.064	177.6	8.2	4.17	5.1	0.043
III	Lenzing Lyocell 3.3	742.6	2.8	7.05	6.9	0.104	260.1	2.9	4.24	6.5	0.062	187.0	3.4	4.23	4.5	0.044
IV	Lenzing Lyocell 1.7	645.3	2.8	6.22	3.3	0.106	212.9	2.3	3.68	8.1	0.058	193.7	10.0	4.25	9.3	0.046
V	Lenzing Viscose 1.7	569.4	3.5	6.93	9.8	0.082	206.5	6.0	3.75	10.8	0.055	163.8	9.1	4.07	10.3	0.040

From the viscose fibres presented in Table 1, five variants of precursor needed nonwovens were made and the same technological parameters were used, namely: the web had an orthotropic structure with a surface mass of 900 g/m², thanks to a laboratory carding machine; the fibres were needled with an Asselin needling machine, using the same number of needlings and needling depth. The active nonwovens were made in two stages. At the first stage, precursor nonwovens were subjected to pyrolysis in an atmosphere of vapours and gases up to a final temperature of 600°C. Thermal treatment was carried out by the periodical method in a chamber reactor at a low rate of temperature increment. At the second stage, carbon nonwovens were activated at a temperature of 850°C. Oxidation was conducted by means of the physicochemical method using steam as an activator until approx. 50-60% of the carbon substance was gasified (a mass loss of 0.75 l/h). The amount of oxidant used was significantly higher than the stoichiometric one. Activation was performed in a periodically operating horizontal tube reactor. The non-

uniformity of all types of nonwovens were assessed based on the value of the coefficient of variation in their mass and thickness.

The morphology of the nonwovens was studied on the basis of the binding standards [2]: the surface mass according to PN-EN 29073-1, the thickness according to PN-EN 2907-3, and the apparent density according to PN-73/P-04613. The characteristics of the carbon and active precursor nonwovens are presented in Table 2.

From the point of view of the use of active nonwovens for electrode materials, their resistance is a very important feature. Investigations into the through resistance (in perpendicular to the surface of the specimens) and the surface resistance (along the surface) were carried out based on the standards PN-EN 1149-2 and PN-92/E-05203. The electrode diameter was 89 mm and its mass 1430 g, whereas the value of pressure over the measuring period was determined by predicting the working conditions of the material tested. The results obtained

are presented in Tables 3 and 4, and in a graphic form in Figures 1, 2 and 3.

Analysis of the Results

The non-uniformity of physical features of the precursor fibres was on average less than 7 per cent. The process of carbonisation and activation of the nonwovens had no effect on the uniformity of mass and thickness of carbon and active nonwovens. It is of the same order as that of the precursor nonwovens.

As can be seen from the results shown in the tables and figures, the through resistance of the precursor nonwovens is of the order of 10¹⁰ ohm. After the precursor nonwovens have been carbonated, the carbon nonwovens are characterised by a through resistance of an order of 10⁶ ohm, i.e. smaller by four orders of magnitude. The activation process results in a decrease in the through resistance of active nonwovens by another six orders of magnitude, down to the value of less than one ohm.

Precursor fibres are dielectrics whose resistance largely depends on the size and orientation of crystalline areas in a fibre during its formation [4,5], the chemical composition and content of functional groups on the fibre surface, and the temperature-time conditions during the formation. The results obtained reveal the following differences between the structure and the manner of formation of the types of cellulose fibres studied.

As far as precursor nonwovens are concerned, one can see that the type of raw material from which they were made has an effect on the magnitude of their resistance. And so, the nonwovens made from Lyocell have the highest resistance, while those formed from Viscose fibres the lowest. This refers both to through and surface resistance.

The non-uniformity of through and surface resistance of the precursor nonwovens, characterised by the value of the coeffi-

Table 3. Through resistance of carbon and active precursor nonwovens.

Variant number	Type of fibres	Through resistance of nonwovens				
		Precursor		Carbon	Active	
		MΩ x 10 ⁴	V, %	MΩ	Ω	V, %
I	Lenzing Modal 3.3	1.14	8.1	12.0	0.74	6.9
II	Lenzing Modal 1.7	1.03	9.9	4.21	0.71	4.6
III	Lenzing Lyocell 3.3	1.94	11.7	2.70	0.83	5.1
IV	Lenzing Lyocell 1.7	2.23	7.1	2.46	0.75	6.8
V	Lenzing Viscose 1.7	0.80	11.3	0.42	0.74	8.4

Table 4. Surface resistance of the carbon and active precursor nonwovens.

Variant number	Type of fibres	Surface resistance of nonwovens				
		Precursor		Carbon	Active	
		MΩ x 10 ⁴	V, %	MΩ	Ω	V, %
I	Lenzing Modal 3.3	1.93	4.4	13.5	1.04	5.4
II	Lenzing Modal 1.7	1.78	5.9	6.57	0.98	4.9
III	Lenzing Lyocell 3.3	3.12	9.5	3.15	1.08	6.2
IV	Lenzing Lyocell 1.7	3.81	6.4	3.24	1.05	5.5
V	Lenzing Viscose 1.7	1.35	10.1	0.44	0.91	7.2

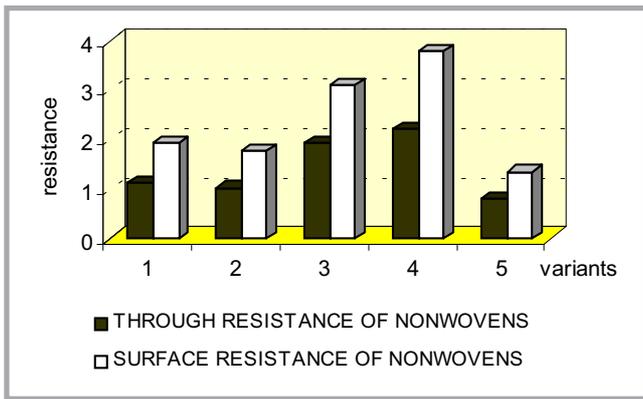


Figure 1. Through and surface resistance of precursor nonwovens in $M\Omega \times 10^4$.

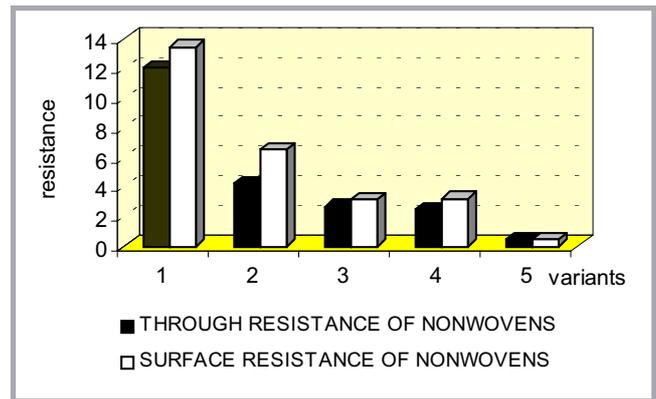


Figure 2. Through and surface resistance of carbon nonwovens in $M\Omega$.

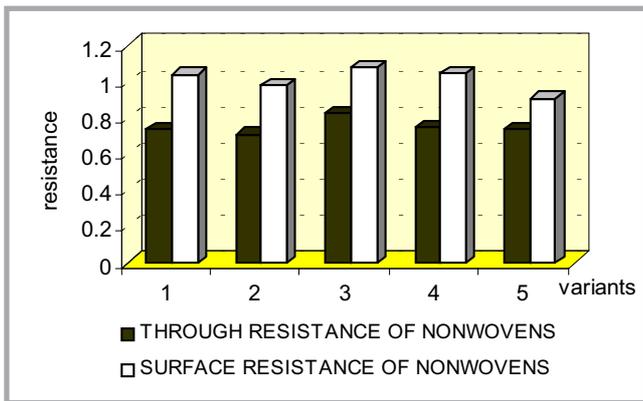


Figure 3. Through and surface resistance of active nonwovens in Ω .

cient of variation, does not differ from the non-uniformity of the physical properties studied, and is significantly below 10%.

In the case of carbon nonwovens, the internal structure of carbon fibres not yet stabilised after the process of carbonisation, has a decisive effect on the non-uniformity of resistance of nonwovens. After the process of carbonisation of the precursor nonwovens at a temperature of 600°C , their resistance decreases by four orders of magnitude down to about 10^6 ohm. This is related to the rearrangement of the carbon matrix structure during pyrolysis aimed at the cyclisation and formation of ordered graphen structures [6,7]. The ordered conducting areas of small resistivity co-exist with amorphous regions of low conductance [8]. In such a multi-conducting system, the conducting phase begins to predominate with an increase in treatment temperature. In different fibres the degree of formation of a conducting structure depends on the initial temperature of the thermal viscose decomposition and the depth of further changes. This stage is the most intensive over the range of temperatures of $600\text{-}900^\circ\text{C}$ [11]. The smallest resistance of Viscose 1,7 fibres can be explained by their highest reactivity and the lowest temperature of thermal decomposi-

tion which results in the most advanced rearrangement of the carbon matrix structure. This is also the consequence of their smallest resistance as a precursor fibre.

Viscose fibres are classical fibres of a bark structure. Their outer layer, of a large edge line responsible for electrical conductance, manifests a significantly greater structural anisotropy, compared with the remaining fibres, which in consequence, leads after thermal treatment to the formation of a highly-ordered, conducting carbon layer. According to Backona [9] and others [10], this layer, unlike the inner part of a fibre, undergoes even partial graphitisation.

In view of the scatter of the results obtained, the effect of the type of precursor material upon the magnitude of resistance of carbon nonwovens cannot be evaluated unambiguously. The very low resistance of active fibres is a consequence of the rearrangement of the internal structure of the fibres and the gasification of a considerable part of the amorphous components. The fibres obtained during activation at a temperature of 850°C thus have a highly-developed internal structure and a large number of conducting cyclic fragments in the form of graphen layers. The

internal surface also has a considerable number of surface functional groups, of both acidic (among others, carboxyl, carbonyl and hydroxyl) and basic character, which has a beneficial effect on a decrease in the fibre resistance. Significant differences in resistance occurring in carbon fibres were clearly equalised, testifying to a stage of the internal arrangement similar to that of all the fibres subjected to activation. Active nonwovens made from precursor raw material of the Lyocell type are characterised by a slightly higher through and surface resistance. The differences which still exist seem to result from the primary structure of precursor fibres. The magnitude of non-uniformity of the resistance of active nonwovens corresponds to that of precursor nonwovens. In this case, however, it can be seen that the values of resistance for the particular variants are close to one another.

It should also be noted that thinner fibres (1.7 dtex) have a smaller resistance, which can result from the greater amount of them in the nonwoven, hence the greater number of contacts between them, and the greater total outer area of the fibres which conducts electric current.

These observations allow us to state that the resistance of carbon fibres activated at a temperature of 850°C is low, and depends to a limited extent on the type of precursor fibres. The temperature of the treatment is even more important. Thus, if a further decrease in the resistance of active fibres as an electrode material in electrochemical capacitors is to be obtained, studies should be carried out to determine and design a morphological structure of nonwoven that allows the number of electric contacts between single fibres to be increased and their quality to be improved.

Conclusions

- The resistances of the precursor non-wovens are significantly differentiated, which results in their structural and morphological arrangement after pyrolysis. The resistance values, which decreased 10^4 times, are a measure of the degree of restructurisation of the fibres' carbon matrix at the temperature of pyrolysis, and at a smaller degree conditioned by the preliminary resistance.
- Further heating and activation of the carbon fibres leads to a further significant decrease in the resistance of active carbon fibres and to an equalisation of their values which do not depend on the kind and thickness of the precursor fibres.
- The low through resistance (below 1 ohm) and low surface resistance (about 1 ohm) allow us to state that the regenerated cellulose fibres tested meet the condition accepted for electrode materials, and that their parameters will not be the reason for significant power loss during the working periods of the capacitors.



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