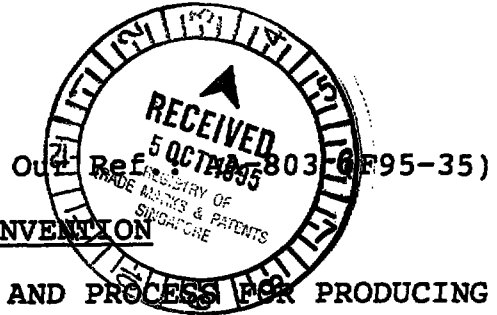




TITLE OF THE INVENTION

ELECTRIC DOUBLE LAYER CAPACITOR AND PROCESS FOR PRODUCING
A POLARIZATION ELECTRODE FOR THE ELECTRIC DOUBLE LAYER
CAPACITOR

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to an electric double layer capacitor having a large electrostatic capacitance and a high working voltage, and a process for producing a polarization electrode for the electric double layer capacitor.

DISCUSSION OF BACKGROUND

To make an electric double layer capacitor small in size and light in weight, it is necessary to increase the amount of storage energy per unit volume of the capacitor (hereinafter referred to as the energy density). The storage energy of a capacitor is proportional to the electrostatic capacitance of the capacitor and is proportional to the square of the applied voltage (working voltage). Accordingly, in order to increase the energy density of a capacitor, the electrostatic capacitance per unit volume may be increased, and the capacitor may be made operable at a high working voltage.

Heretofore, in order to obtain an electric double layer capacitor having a large electrostatic capacitance, it has been common to employ activated carbon having a



high specific surface area for the polarization electrode. As the activated carbon having a high specific surface area, it has been common to employ activated carbon prepared by subjecting carbon material to activation treatment by a steam activation method employing steam or by a chemical activation method employing e.g. zinc chloride. However, such activated carbon is not adequate in the electrostatic capacitance density per unit volume when made into a polarization electrode, and deterioration in the performance upon application of a high voltage is quick. Accordingly, it is not suitable for a prospective application where a high energy density is required.

Japanese Unexamined Patent Publication No. 78513/1988 proposes an electric double layer capacitor employing an organic solvent type electrolyte and activated carbon having a high specific surface area, prepared by subjecting petroleum coke to activation treatment by a high temperature activation method employing molten potassium hydroxide. This activated carbon is advantageous in that the energy density can be made higher than the conventional electric double layer capacitor, since the specific surface area is very large. However, its working voltage is at best as low as 2.8 V, and it is desired to improve the working voltage to improve the energy density.

SUMMARY OF THE INVENTION

It is an object of the present invention to solve the above problems in the prior art for electric double layer capacitors and to provide an electric double layer capacitor which has a high working voltage, to which a higher voltage can be applied and which has a high energy density.

The present invention provides an electric double layer capacitor comprising a polarization electrode and an electrolyte capable of forming an electric double layer on the surface of the polarization electrode, wherein the polarization electrode is composed mainly of an activated carbon prepared by subjecting carbon material made from at least one resin selected from the group consisting of phenol resins, furan resins and polyacrylonitrile resins, as the starting material, to an activating method employing potassium hydroxide in a molten state, and the electrolyte is an organic solvent type electrolyte.

Further, the present invention provides a process for producing a polarization electrode for an electric double layer capacitor, which comprises carbonizing at least one resin selected from the group consisting of phenol resins, furan resins, and polyacrylonitrile resins to form a carbon material, converting the carbon material to activated carbon by an activation method in which the carbon material is heated together with molten potassium hydroxide at a temperature of from 600 to 1,000°C, adding

a binder and an electroconductive material to a powder of the activated carbon to obtain a mixture, and fixing the mixture to a current collector.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the electric double layer capacitor of the present invention, activated carbon prepared by subjecting carbon material made from a certain specific resin as the starting material, i.e. at least one resin selected from the group consisting of phenol resins, furan resins and polyacrylonitrile resins, to an activating method employing potassium hydroxide in a molten state, is used for the polarization electrode.

This activated carbon is obtained by heating the carbon material together with potassium hydroxide in a mixed state, so that the carbon material is activated in the presence of molten potassium hydroxide. This activated carbon has features such that the specific surface area is large, the amount of functional groups at the surface is less than that of conventional activated carbon obtained by subjecting the above-mentioned petroleum coke to an activation method employing molten potassium hydroxide, and heavy metal impurities derived from the starting material are little.

The present inventors have found it possible to increase the working voltage of an electric double layer capacitor by using for the polarization electrode an activated carbon prepared by subjecting the above-

mentioned specific carbon material to an activation treatment employing molten potassium hydroxide. On the basis of this discovery, an electric double layer capacitor which has a high electrostatic capacitance and a high working voltage, has been accomplished. The reason why an electric double layer capacitor having a high working voltage can be obtained, is believed to be attributable to the fact that the deterioration in the performance upon application of a high voltage due to the presence of heavy metal impurities or functional groups at the surface of activated carbon, can be substantially reduced.

Phenol resins, furan resins and polyacrylonitrile resins as starting materials for such carbon material are common in that the carbonization yield after the carbonization treatment is high. This may be attributed to the fact that each of them has many double bonds in its molecular structure. Among these resins, phenol resins are most suitable in that the properties of activated carbon thereby obtained are good, and the price is low. Carbonization treatment of such resins is preferably conducted in a non-oxidizing atmosphere at a temperature of from 500 to 1,200°C. If the temperature for carbonization treatment is lower than 500°C, it takes long time for the carbonization treatment. On the other hand, if the temperature for carbonization treatment is higher than 1,200°C, it tends to be difficult to obtain

activated carbon having a large specific surface area. As conditions for the activating treatment utilizing molten potassium hydroxide, which are influential over the specific surface area and the pore size of activated carbon, the amount of potassium hydroxide to be mixed with the carbon material and the temperature for the activation treatment are important. To obtain activated carbon having preferred properties, it is advisable to mix potassium hydroxide in an amount of from 2 to 6 parts by weight per one part by weight of the carbon material, preferably from 2.5 to 4.5 parts by weight per one part by weight of the carbon material. If the amount of potassium hydroxide mixed to one part by weight of carbon material is at least two parts by weight, a good contact state of the carbon material with the molten potassium hydroxide can be secured during the activation treatment, whereby the carbon material can be swiftly activated. However, if the amount of potassium hydroxide mixed to a predetermined amount of the carbon material is too much, the amount of the mixture to be treated will increase, whereby the activation treatment capacity of the activation treatment furnace will decrease, and the amount of wasted potassium hydroxide will increase. Therefore, the amount is preferably at most 6 parts by weight.

The temperature for activation treatment of the carbon material is preferably from 600 to 1,000°C, more

preferably from 700 to 900°C. If the activation treatment temperature is low, it takes long time for the activation treatment to obtain activated carbon having a large specific surface area. Therefore, the activation treatment temperature is preferably at least 600°C. On the other hand, if the activation treatment temperature is too high, pore size of the activated carbon tends to be large, whereby the electrostatic capacitance per unit volume of the polarization electrode decreases. Besides, wearing of the material of the furnace used for the activation treatment increases, and the energy consumption by the activation treatment furnace will also increase. Therefore, the activation treatment temperature is preferably at most 1,000°C.

The larger the specific surface area of activated carbon is, the larger will be the electrostatic capacitance of the electric double layer per unit weight of the activated carbon. However, if the activation proceeds too much, and the specific surface area becomes excessive, the pore volume of the activated carbon increases, whereby the apparent density of the electrode decreases. If the apparent density of the activated carbon decreases, the electrostatic capacitance per unit volume of the polarization electrode decreases. Therefore, the specific surface area of the activated carbon is controlled preferably within a range of from 1,500 to 2,500 m²/g. If the specific surface area of the

activated carbon is within this range, it is possible to obtain a polarization electrode having a large electrostatic capacitance per unit volume.

To prepare the polarization electrode, it is necessary to mold and fix the electrode material composed mainly of the activated carbon on a current collector in a state where the electrical connection is maintained. For this purpose, it is possible to employ a conventional method for molding and fixing a polarization electrode.

In the present invention, in order to secure a high working voltage of the capacitor, an organic solvent type electrolyte having a high decomposition voltage is used. As the electrolyte salt for the organic solvent type electrolyte, it is preferred to employ a salt made of a combination of a quaternary onium cation such as a quaternary ammonium ion of the formula R_4N^+ or a quaternary phosphonium ion of the formula R_4P^+ (wherein R is an alkyl group of the formula C_nH_{2n+1}) and an anion such as BF_4^- , PF_6^- , ClO_4^- or $CF_3SO_3^-$. For the organic solvent type electrolyte, it is preferred to use an organic solvent having a low water content, so that a high decomposition voltage will be obtained.

As the organic solvent for the electrolyte, it is preferred to use at least one member selected from the group consisting of carbonates such as propylene carbonate, butylene carbonate, diethyl carbonate and ethylmethyl carbonate, lactones such as γ -butyrolactone,

sulfolane and its derivatives, since it is thereby possible to obtain an electrolyte having a high decomposition voltage.

Now, the present invention will be described in further detail with reference to Examples (Examples 1 to 13) and Comparative Examples (Examples 14 to 19), but it should be understood that the present invention is by no means restricted by such specific Examples.

Using various carbon materials having an average particle size of 2 to 3 mm obtained by carbonization treatment at about 700°C of resins as identified in Table 1 as starting materials (A: phenol resin, B: furan resin, C: polyacrylonitrile resin, D: petroleum coke, E: coconuts shell, F: sawdust) and three types of activation methods (G, G' and G": molten KOH activation methods, H: steam activation method, I: zinc chloride activation method), activated carbons having the specific surface areas (unit: m^2/g) as shown in Table 1, were obtained. The conditions G, G' and G" for activation treatment of activated carbon employing molten potassium hydroxide are such that the amounts of potassium hydroxide mixed to one part by weight of the carbon material were 3 parts by weight, 2.5 parts by weight and 2.5 parts by weight, respectively, and the activation temperatures were 800°C, 800°C and 700°C, respectively.

To 80 wt% of a powder (the average particle size was about 10 μm in each case) obtained by pulverizing each of

the activated carbons obtained by the above activation methods, 10 wt% of polytetrafluoroethylene as a binder and 10 wt% of carbon black as an electroconductive material to improve the conductivity of polarization electrode, were mixed. Then, ethanol was added to this mixture, followed by kneading and formed into a sheet. Then, the sheet was further rolled to a thickness of 0.6 mm and dried at 150°C, and then punched into a disk having a diameter of 12 mm.

This disk having a diameter of 12 mm was bonded by a carbon type conductive adhesive to the inside of each of a stainless steel case and a stainless steel cover, which were current collectors and at the same time container parts for a coin-shaped capacitor cell, and both were heat treated in vacuum to remove moisture, etc. contained in the both polarization electrodes. In an organic solvent having a small moisture content (at most 50 ppm in each case) as identified in Table 1 (PC: propylene carbonate, BC: butylene carbonate, SL: sulfolane), an electrolyte $(C_2H_5)_4NBF_4$ was dissolved at the concentration (unit: mol concentration) as shown in Table 1 to prepare an organic solvent type electrolyte. This organic solvent type electrolyte was sufficiently impregnated to the both polarization electrodes composed mainly of the activated carbon, and at the same time, to a separator sheet made of a nonwoven fabric of polypropylene fiber placed between the two polarization

electrodes. They are crimp sealed in the stainless steel coin-shaped container to obtain a coin-shaped electric double layer capacitor having a diameter of 18.4 mm and a thickness of 2.0 mm.

With respect to each electric double layer capacitor, the initial electrostatic capacitance (unit: F) and the internal resistance (unit: Ω) were measured. Then, each capacitor was put in a thermostat at 70°C, and a voltage of 3.0 V was applied for 1,000 hours, whereby the electrostatic capacitance (unit: F) and the internal resistance (unit: Ω) upon expiration of 1,000 hours were measured. By comparing the degree of the performance change between before and after the operation, the long term working reliability of the respective capacitor under a high voltage (3.0 V) application condition was evaluated on an accelerated basis. The evaluation results of the respective capacitors are shown in Table 1.

Table 1

Example	Conditions for the production of capacitors					Initial properties		Properties after application of the voltage	
	Starting material for the carbon material	Activation method	Specific surface area	Organic solvent	Electrolyte concentration	Electrostatic capacitance	Internal resistance	Electrostatic capacitance	Internal resistance
1	A	G	1900	PC	1.0	3.3	4.8	2.9	8.0
2	A	G	1900	PC	1.0	3.3	4.7	2.9	8.2
3	A	G	1900	BC	0.8	3.1	5.5	2.7	10.7
4	A	G	1900	SL	0.5	2.9	7.9	2.8	12.3
5	A	G	2200	PC	1.0	3.2	4.4	2.8	8.3
6	A	G	2500	PC	1.0	3.1	4.6	2.7	8.2
7	A	G	2800	PC	1.0	2.9	4.7	2.5	9.1
8	A	G	1500	PC	1.0	2.5	4.9	2.2	10.5
9	A	G	1100	PC	1.0	2.3	5.1	2.0	12.4
10	C	G	1600	PC	1.0	2.6	4.9	2.1	11.9
11	B	G	1800	PC	1.0	2.8	4.8	2.3	10.8
12	A	G'	2000	PC	1.0	3.5	4.7	3.1	8.1
13	A	G''	2100	PC	1.0	3.6	4.7	3.0	12.5
14	D	G	1900	PC	1.0	3.1	4.9	2.0	13.7

Table 1 (continued)

Example	Conditions for the production of capacitors					Initial properties		Properties after application of the voltage	
	Starting material for the carbon material	Activation method	Specific surface area	Organic solvent	Electrolyte concentration	Electro-static capacitance	Internal resistance	Electro-static capacitance	Internal resistance
15	D	G	2800	PC	1.0	2.7	4.8	1.7	14.5
16	D	G	1100	PC	1.0	2.0	5.2	1.1	18.4
17	E	H	1800	PC	1.0	1.9	4.7	1.3	11.0
18	A	H	2500	PC	1.0	2.1	4.8	1.5	9.6
19	F	I	1100	PC	1.0	1.6	5.3	0.9	20.8

As is apparent from the evaluation results shown in Table 1, with the electric double layer capacitors of the present invention, the working voltage is high, deterioration in the properties is little even after application of a high voltage at a level of 3.0 V for 1,000 hours, and the electrostatic capacitance is large. Accordingly, according to the present invention, it is possible to provide an electric double layer capacitor which has high reliability and a high energy density.



CLAIMS:

1. An electric double layer capacitor comprising a polarization electrode and an electrolyte capable of forming an electric double layer on the surface of the polarization electrode, wherein the polarization electrode is composed mainly of activated carbon prepared by subjecting carbon material made from at least one resin selected from the group consisting of phenol resins, furan resins and polyacrylonitrile resins, as the starting material, to an activating method employing potassium hydroxide in a molten state, and the electrolyte is an organic solvent type electrolyte.
2. The electric double layer capacitor according to Claim 1, wherein the organic solvent type electrolyte contains a quaternary ammonium salt or a quaternary phosphonium salt.
3. The electric double layer capacitor according to Claim 1 or 2, wherein the activated carbon has a specific surface area of from 1,500 to 2,500 m²/g.
4. A process for producing a polarization electrode for an electric double layer capacitor, which comprises carbonizing at least one resin selected from the group consisting of phenol resins, furan resins, and polyacrylonitrile resins to form a carbon material, converting the carbon material to an activated carbon by an activation method in which the carbon material is heated together with molten potassium hydroxide at a

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- 16 -

temperature of from 600 to 1,000°C, adding a binder and an electroconductive material to a powder of the activated carbon to obtain a mixture, and fixing the mixture to a current collector.

5. The process for producing a polarization electrode for an electric double layer capacitor according to Claim 4, wherein the activation treatment is carried out by mixing the potassium hydroxide and the carbon material so that the weight ratio of potassium hydroxide/carbon material would be from 2 to 6.

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