Study of Peat Fillers for their Potential Use in Electric Energy Storage Devices

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Abstract. The article discusses the pros and cons of modern devices for power accumulating and its storage (supercapacitors). The author analyses porous carbon materials traditionally used as fillers in such devices. The presented main physical and chemical properties of peat allow the author to propose a working hypothesis about the possibility of using peat sorbents in supercapacitors. This is possible due to the high specific surface area of peat and by the presence of particles with a double electric layer (micelles) in it. For the first time ever, it was experimentally established that the use of a bog peat sorbent instead of activated carbon as a porous material makes it possible to multiply the voltage during self-discharge of an experimental model of a supercapacitor. The size of the peat sorbent fractions does not significantly affect the self-discharge process. However, there is a slight improvement in the performance of the device when using the fractions under 1.25 mm. The use of peat raw materials with a high degree of decomposition significantly improves the characteristics of the experimental model at a charging voltage of 10 V.

1 Introduction

The promising use of organic biogenic materials in devices for the accumulation and storage of electrical energy, as well as chemical energy-containing compounds stems from the physical and chemical properties of their individual structural units and, consequently, of the whole system. First of all, this is ensured by high porosity, which allows to sorb and retain (bind) various types of solid, liquid and gaseous energy carriers. The use of electrokinetic properties of peat systems [1-3] can become a separate direction within this scientific field.

Currently, there is a fairly large number of publications [3-6] on the application of porous dispersed materials with high specific surface area in devices for the accumulation and storage of electrical energy – supercapacitors. These are electrical devices, capable of giving a huge amount of energy in a short period of time that are used in various fields of electronics and electrical engineering. The main advantages of supercapacitors over conventional capacitors are their ability to combine high power and significant charge capacity, extremely fast charge accumulation, ability to withstand an almost unlimited number of charge-discharge cycles without loss of operational properties, polarity reversal, and other equally important characteristics [3, 4].

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Accumulation and storage of charge in such capacitors occurs in a double electric layer [7], which appears in the “electrode - electrolyte” phase boundary. Thus, materials for these devices should possess the following properties: high electrical conductivity, developed specific surface area, availability of a porous structure for electrolyte ions, low density, ease of formation, and other properties that make it possible to substantiate the economic efficiency of their use. Currently, carbon materials (activated carbon, graphite, carbon aerogels, meso- and macroporous carbon, single-walled and multi-walled nanotubes), transition metal oxides, and conducting polymers are used as such materials [3-5]. Many of them are quite effective, but have a high cost.

Recent years saw the first publications related to the substantiation of the possibility of using porous carbon from biomass as a functional material in supercapacitors. Moreover, it can be used both as an absorbent and as an electrode material. For example, the study [6] investigates the possibility of using fallen leaves as such biomass. However, in this case as well, this method uses the hydrothermal activation with the transformation into carbon microspheres, followed by the production of a porous carbon material. Thus, we eventually deal with the same carbon, and it would be more expensive than the conventional method.

Supercapacitors use aqueous solutions of salts and organic electrolytes as electrolytes. For symmetrical capacitors in aqueous electrolytes, the maximum operating voltage is limited to 0.7-0.8 V (with an estimated value of 1.23 V). When the voltage rises, the electrolyte decomposes. In organic electrolytes, the voltage limit can be increased to 2.7 V [6]. From this point of view, organic electrolytes are more promising for industrial applications, despite the lower capacity of the electrodes in comparison with the aqueous electrolytes.

2 Review

Peat is distinguished by an extremely variable disperse composition and the presence of various groups of chemical compounds, since it consists of plant residues of cellulose polymers and products of their natural biochemical decomposition. According to Lishtvan [8-10], the main kinetic units of the peat system are aggregates and associates of macromolecules of these compounds, which are permeable to water molecules and ions. They constitute the hydrophilic part of the organic matter of peat. At the same time, peat also contains ordered areas of decomposition products, which, in combination with the aggregates of bituminous substances, are difficult for water penetration. During thermal modification of peat, the content (amount) of bituminous components in its organic matter can increase depending on the process parameters [11-13].

Macro- and microstructural elements of peat are formed from the aggregates and associates, as well as elements of a higher order due to the forces of different nature (mainly van der Waals interactions and hydrogen bonds). As a result of these complex processes, intra- and inter-aggregate structures are formed with varying degrees of localization, which properties depend on many factors [8-10]. The main factors are the composition of peat-forming plants, the degree of their biochemical decomposition (degree of decomposition R_p), the conditions of peat formation and the chemical composition of water. Thus, in its natural moisture-saturated state, the peat system is a complex multicomponent polydisperse (multi-fractional) semi-colloidal-high molecular system. Moreover, the presence of hydrophilic semi-colloids, stabilized hydrophobic compounds, and dispersions of high-molecular compounds in it forms its specific properties, which significantly distinguish peat from typical colloidal heterogeneous systems.

Peat particles are electrically charged and located in a medium with a high permittivity. The charge is caused by the dissociation of the functional groups of macromolecules forming the particles, as well as by the selective adsorption of cations and anions by the dispersion medium [14-16]. It is known [17] that particles of the dispersed phase ranging from 10 nm to 1 µm, carrying charges and ions of the opposite sign and diffusely distributed in the dispersion medium, are called micelles. They consist of an aggregate, a nucleus and a particle (Fig. 1, 2). In this regard, peat particles corresponding to the size of the colloidal fraction also belong to the category of micelles [2, 14, 15], which is associated with the presence of a double electric layer.

The main difficulty in predicting the course of electrokinetic processes in peat systems is that colloids in peat can be organic, mineral, and organomineral. Most of the colloids in the peat systems with low and medium ash content are organic. They are represented by groups of humic substances and are characterized by high dispersion. High ash content causes preconditions for the formation of mineral colloids in the system, consisting of finely dispersed clastic materials (quartz, mica, secondary minerals, etc.). Organomineral colloidal complexes are mainly compounds of humic substances with clay minerals.

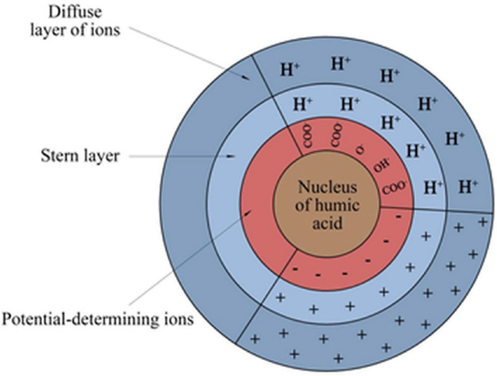

Fig. 1. Scheme of micelle structure – acidoid (N.I. Gorbunov).

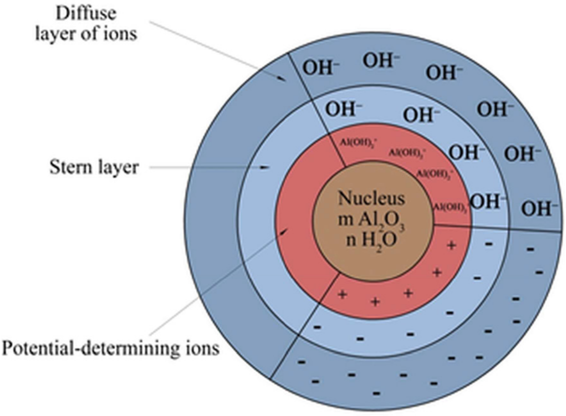

Fig. 2. Scheme of micelle structure – basoid (NP Remezov).

The sign of the electric charge of colloidal particles divides them into acidoids (Fig. 1), basoids (Fig. 2) and ampholithoids. Colloids carrying a negative charge are called acidoids (in the potential-determining layer – anions, in the diffuse layer – cations). Basoids are positively charged colloids carrying cations in the potential-determining layer and anions in the diffuse layer. Ampholitoids are able to change their charge depending on the reaction of the environment. Most colloids of peat systems are acidoids, since they mainly contain humic substances, the amount of which is determined by the degree of decomposition.

Thus, the presence of a double electric layer in peat systems determines their electrokinetic properties, and the porous structure provides high sorption characteristics [1-3, 14-16], which is the basis to study the prospects for its use in devices for accumulating and storing electrical energy.

The aim of this work is to carry out a comparative analysis of the effects of different types of modified peat fillers and activated carbon-based fillers on the voltage change during self-discharge of a model electric energy storage device (supercapacitor).

3 Methods used

Activated charcoal for domestic water filters with a particle size of 2.5 to 5 mm was used as a standard carbon filler. Sorbents made of modified bog magellanicum peat with decomposition rate $R_P = 5$ % and cottongrass-sphagnum peat with $R_P = 30$ % were used as peat fillers. The experiments were carried out with sieve-fractionated and multi-fractionated peat fillers with particle sizes: $d < 0.63$; $0.63 < d < 1.25$; $1.25 < d < 2.5$; $2.5 < d < 5$ mm.

In the experiments the condition of equal masses in dry matter of coal and peat fillers was maintained. A saturated aqueous sodium chloride solution was used as an electrolyte.

Additionally, graphite electrodes (SIEMENS production) with density 1252 kg/m^3, length 100 mm and diameter 9 mm were used in experiments.

The experimental setup (Fig. 3) included a polyethylene jar (1) in which carbon (control sample) or peat filler (2) (experimental sample) were placed and electrodes (3) were installed. The jar was divided into two equal parts by a filter paper separator (4). Then the electrolyte was poured into the jar. The saturation of peat filler in the experimental setup with electrolyte differed from the carbon filler in that it was preliminarily brought to the state of full moisture capacity (by aqueous saline solution) in a Buechner funnel, and only then was placed in the jar.

The supercapacitor model was charged from a laboratory direct current source (5) by closing the key (6). The discharge voltage was measured after switching off the current source, using a voltmeter (7) (DT830B multimeter) after closing the key (8). The self-discharge process was monitored for 1 hour.

The first series of experiments investigated the operation of devices with activated carbon and peat sorbent using an aqueous NaCl solution as an electrolyte in the following modes:

1. Charging time (t_{ch}) = 1 min, voltage (U) = 1 volt, current (I) = 0.2 ampere;
2. $t_{ch} = 5$ min, $U = 1$ V, $I = 0.2$ A;
3. $t_{ch} = 1$ min, $U = 1$ V, $I = 1$ A;
4. $t_{ch} = 5$ min, $U = 1$ V, $I = 1$ A.

This approach allowed us to analyse the dependence of self-discharge voltage on charging time and current strength at a fixed voltage in accordance with the limits for its value presented in the paper [6].

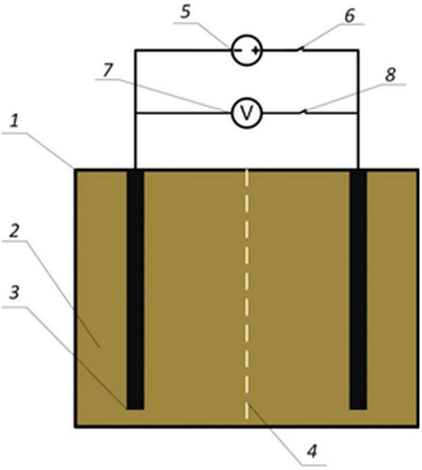

Fig. 3. Diagram of the experimental setup – the supercapacitor model (here and in the other figures – explanations in the text).

The second series of experiments studied the operation of devices with different fractions of peat filler with a change in some geometric dimensions of the supercapacitor model (the distance between the electrodes).

The third series of experiments analysed the use of peat with a high degree of decomposition as a basis for peat filler. In addition, the charge voltage of the supercapacitor model was 10 V. Such voltage values were adopted in order to study the possibility of increasing it in an experimental setup, as well as to assess the probability of electrolyte decomposition in a peat matrix.

4 Results and Discussion

A comparative analysis of the effect of the filler on the self-discharge of the experimental setup shows that the use of the bog peat sorbent as a porous material (R_T = 5 %) radically increases the voltage throughout the entire measurement period. For example (Fig. 4), depending on the charging current, the voltage is higher in the device with peat filler from 3.6-5 times (I_{ch} = 0.2 A, curves 1, 2) to 1.65-5.75 times ((I_{ch} = 1.0 A, curves 1', 2'). Moreover, a raise in the charging current by 5 times also increases the voltage in it by 15-50%, which noticeably distinguishes the peat filler from the standard (coal) filler in absolute terms (in relative terms, they are approximately equal).

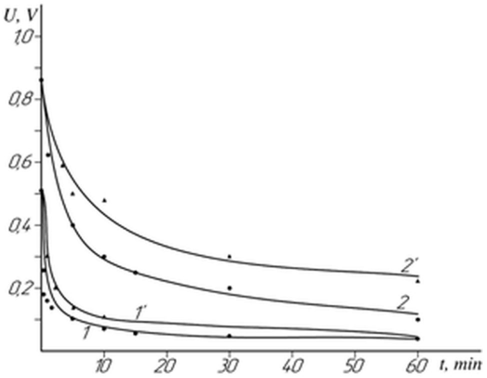

Fig. 4. Self-discharge of the device model for accumulating electrical energy (charge time is 1 minute) with a filler in the form of: *1*, *1'* – activated carbon; *2*, *2'* – sorbent from bog peat (R P = 5 %).

Increasing charging time to 10 minutes (Fig. 5) improves the performance of experimental studies in both cases (activated carbon and peat sorbent). However, this improvement is especially noticeable only in the model of a supercapacitor with the peat sorbent. Firstly, the influence of the device charging current is minimized. Secondly excess between the maximum (start of the experiment, 0 minutes) and minimum voltage indicators (end of the experiment, 60 minutes) is 2.54-3.35 times for the peat sorbent and 7.7-8.6 times for the activated carbon. In the previous case (Fig. 4) it differed by 3.8-5.6 and 7.6-13 times, respectively. And, thirdly, higher voltages are achieved throughout the entire discharge time when the external charger is disconnected (compare Fig. 4 and Fig. 5).

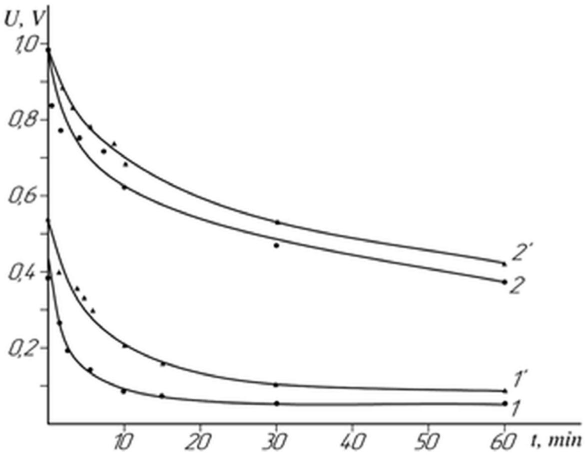

Fig. 5. Self-discharge of the device model for accumulating electrical energy (charge time is 10 minutes) with a filler in the form of: *1*, *1'* – activated carbon; *2*, *2'* – sorbent from bog peat (R P = 5 %).

To assess the effect of particle size on voltage in the setup, a series of experiments were carried out with the peat filler of different fractions (Table 1). The analysis shows that the size of the fractions has little effect on the self-discharging process. A slight improvement in the performance of the device can be observed when smaller fractions are used. It is noticeable when using the filler with particle diameter below 1.25 mm: during the whole period of self-discharging for these fractions, higher voltage values (from 20 % and above) are maintained. This is likely due to the increased content of humic substances, which create conditions for the formation of more micelles (acidoid). But, it is needed to perform further detailed studies using medium and high decomposition peat to substantiate this assumption. At the moment, the use of fine-dispersed fractions of the peat has no great prospects due to the rather energy-consuming methods of their extraction from the total volume of peat raw materials (e.g., milled peat), which are not proportional to the improved quality characteristics of the device.

Table 1. Study of the self-discharge process of the device model for accumulating electrical energy, depending on the size of peat filler particles (t_{ch} = 1 min; I_{ch} = 1.0 A; distance between electrodes – 40 mm).

Time of self-discharge (*t*), min	**Voltage (*U*), V, when using fractions of peat filler (*d*), mm**			
	less than 0.63	0.63-1.25	1.25-2.5	2.5-5.0

0	0.83	0.82	0.75	0.8
1	0.56	0.56	0.45	0.45
2	0.48	0.47	0.34	0.35
3	0.44	0.41	0.29	0.29
5	0.39	0.35	0.23	0.23
10	0.33	0.27	0.17	0.17
15	0.29	0.24	0.15	0.15
30	0.23	0.18	0.13	0.13
60	0.16	0.13	0.11	0.12

An important part of substantiating the models of devices for the accumulation and storage of electrical energy is to study the dependence of the main parameters on the geometric dimensions of their design elements. In this connection, it was necessary to evaluate the influence of the distance between the electrodes on the studied processes, when the volume of the device remained the same. To solve this problem, two identical experimental models were made which differed only in the distances between the electrodes: 40 and 100 mm. To increase the objectivity of the evaluation experiments were carried out with the peat fillers of two different size fractions: $d < 0.63$ mm and $d = 2.5\text{-}5.0$ mm (Tables 2 and 3).

Table 2. Study of the self-discharge process of the device model for accumulating electrical energy (distance between electrodes – 100 mm).

***t*, min**	**Particle size of peat filler (*d*), mm**							
	less than 0.63				from 2.5 to 5.0			
	charging time, min (charging current I_{ch} = 0.2 A)		charging time, min (charging current I_{ch} = 1.0 A)		charging time, min (charging current I_{ch} = 0.2 A)		charging time, min (charging current I_{ch} = 1.0 A)	
	1	5	1	5	1	5	1	5
0	0.84	0.84	0.86	0.9	0.79	0.82	0.75	0.88
1	0.53	0.64	0.58	0.72	0.48	0.64	0.47	0.66
2	0.44	0.55	0.5	0.61	0.39	0.57	0.38	0.57
3	0.39	0.5	0.45	0.56	0.34	0.53	0.33	0.52
5	0.33	0.44	0.4	0.49	0.29	0.48	0.29	0.46
10	0.28	0.36	0.35	0.41	0.24	0.41	0.24	0.39

15	0.25	0.33	0.33	0.38	0.22	0.38	0.22	0.35
30	0.23	0.29	0.29	0.33	0.2	0.34	0.19	0.31
60	0.21	0.25	0.27	0.29	0.19	0.3	0.18	0.28

Analysis of the experimental results shows multidirectional dynamics of voltage changes depending on the particle size, time, and magnitude of charging current in the devices. A slight increase in voltage is observed in some experiments with the supercapacitor models with 100 mm electrode spacing and mainly when they are charged for 5 minutes with 0.2 A and 1.0 A currents.

But numerical values of these variations are insignificant and do not favour any of the experimental models. When a power consumer (an electric motor from a CD drive of a personal computer with resistance 12,8 Ohm) was connected to the supercapacitor model, it didn't launch because of the relatively low voltage and current values.

Table 3. Study of the self-discharge process of the device model for accumulating electrical energy (distance between electrodes – 40 mm).

***t*, min**	**Particle size of peat filler (*d*), mm**							
	less than 0.63				from 2.5 to 5.0			
	charging time, min (charging current I_{ch} = 0.2 A)		charging time, min (charging current I_{ch} = 1.0 A)		charging time, min (charging current I_{ch} = 0.2 A)		charging time, min (charging current I_{ch} = 1.0 A)	
	1	5	1	5	1	5	1	5
0	0.8	0.92	0.83	0.89	0.83	0.77	0.8	0.76
1	0.52	0.66	0.56	0.63	0.44	0.56	0.45	0.57
2	0.4	0.55	0.48	0.52	0.34	0.51	0.35	0.49
3	0.34	0.5	0.44	0.45	0.31	0.47	0.29	0.45
5	0.28	0.43	0.39	0.38	0.25	0.41	0.23	0.39
10	0.21	0.35	0.33	0.3	0.2	0.34	0.17	0.33
15	0.18	0.31	0.29	0.27	0.19	0.31	0.15	0.3
30	0.16	0.27	0.23	0.23	0.17	0.28	0.13	0.26
60	0.14	0.24	0.16	0.2	0.16	0.25	0.12	0.23

To estimate the probability of increasing these values, and to analyse the influence of the degree of peat decomposition on the performance of the supercapacitor, a series of experiments with two types of bog peat with a low and high degree of biochemical decomposition was carried out (Table 4). The difference from previous experiments is the increase of charging voltage by a factor of 10, up to 10 V. The charging current strength remained the same – 1 A.

Analysis of the experimental data revealed the following. When disconnecting the external charger the voltage drops sharply to the range of 2-3 V. And it is characteristic both for slightly decomposed peat and for peat with high values of R_P. It should be noted that in some cases this range was 4-5 V. As these were only fragmentary cases, the fact of their occurrence is noted, but they have not been analysed in this paper.

Further, starting from the time range of approximately 5-10 seconds, the values of the setup with the highly decomposed peat begin to increase throughout the observed time interval (1 hour).

Table 4. Study of the self-discharge process of the device model for accumulating electrical energy.

t, sec.	**0**	**5**	**10**	**20**	**30**	**60**	**120**	**300**	**600**	**1800**	**3600**
Charging time, sec	**Discharge voltage, V**										
Filler, based on bog magellanicum peat with $R_P = 5$ %											
5	2.22	1.79	1.57	1.41	1.3	1.08	0.89	0.74	0.61	0.46	0.38
15	2.91	1.71	1.46	1.28	1.2	0.92	0.73	0.57	0.55	0.48	0.37
60	2.68	2.09	1.89	1.56	1.36	1.36	1.1	0.91	0.76	0.68	0.63
Filler, based on bog cottongrass-sphagnum peat with $R_P = 30$ %											
5	2.77	1.98	1.94	1.78	1.68	1.46	1.33	1.28	122	1.02	0.77
15	2.64	1.7	1.62	1.5	1.39	1.19	1.02	0.85	0.84	0.78	0.76
60	2.69	2.29	2.14	2.01	1.92	1.74	1.57	1.16	0.99	0.99	1.0

Increasing the charging time slightly improves the performance of the setup, but the relationship is not linear. A charging time of 30 to 60 seconds is quite sufficient to ensure the performance of the setup. Moreover, as the charging time approaches one minute, the smell of chlorine appears during the experiment, which indicates the beginning of decomposition of the electrolyte (sodium chloride).

Compared to the data presented in Tables 1 to 3, the voltage is increased throughout the self-discharge period. The 1, 10, 30 and 60 minutes discharge points are especially indicative. At the 1 minute point, the voltage variation range in the setup with low decomposition peat (all other conditions being equal) was 0.45-0.56 V (see Table 3); 10 minutes - 0.17-0.33 V; 30 minutes - 0.13-0.23 V; 60 minutes - 0.12-0.16 V.

Increasing the charging voltage by a factor of 10 leads to a steady voltage increase of 2.7-4.5 in all the above ranges (see Table 4): 1 minute – 1.36 V; 10 minutes – 0.76 V; 30 minutes – 0.68 V; 60 minutes – 0.63 V. Moreover, it is characteristic that although the voltage decreases by a factor of 2.15 in one hour, it still maintains high enough values to sustain (for 30-60 seconds) the operation of the used power consumer.

Replacement of the filler with the sorbent based on the peat with a high degree of decomposition further increases voltage values: firstly, the drop in time interval "1 minute – 1 hour" is 1.74 times; secondly, its index approaches to 1 V, which corresponds to the data of literature sources [6] and is characteristic for the electrolyte used in the device.

4 Conclusions

The obtained experimental data confirm the hypothesis about the positive influence of the highly decomposed colloidal fraction (a potential source of micelles) on electrochemical processes in the investigated systems. To explain the essence of the physicochemical mechanism of these processes, additional research is being carried out using more typical representatives of the peat raw material.

Thus, the paper presented the world's first research results on the use of peat colloidal capillary-porous systems as fillers for electrochemical devices for accumulating and storing electrical energy. The preliminary data analysis allows us to expect the high demand for the received results from the expert community to continue the research in this new non-traditional direction of the use of peat processing products.

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