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A Porous Carbon Material of Organic Raw Materials of Vegetable Nature as an Electrode Component for Electric Double-Layer Capacitors

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In this paper we present investigations of nanoporous carbon materials from organic raw materials of vegetable nature appropriate to be used as an electrode component in supercapacitors with an aqueous electrolyte. For such materials the principal energy - capacity characteristics are determined. Some types of supercapacitors based on the obtained materials are developed and their parameters are investigated.

Keywords: vegetable raw material, supercapacitor, electrode, capacity.

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Introduction

In comparison to conventional primary and secondary power sources, electric double-layer capacitors (EDLCs) are a rather new kind of power sources and initially for practical applications. The important feature of the principle of the operation of EDLCs, a charge accumulation occurs at a double electrical layer [1], in comparison to conventional systems, enabled to consider such power sources as a separate group.

Nevertheless, the basic principle, underlying the operation of EDLCs, remains the same as for the conventional systems: positive charge accumulates at one electrode and a negative charge at another separated from the first by an insulating layer. Thus the accumulation of electrical energy occurs in static form like to a conventional capacitor system. Three main factors, which determine the amount of energy capable to be accumulated in EDLCs, also are the same: the area of electrodes, the distance between them, and electrical properties of an insulating layer between the electrodes. The ways to improve parameters of capacitors were related to these three factors: to increase the area of electrodes, to decrease the distance between them and to improve electrical properties of the insulating layer. The same is correct for EDLCs. Therefore, the capacitance of EDLCs also can be described by the classical formula for planar capacitors:

$$C = \varepsilon S / d, \quad (1)$$

where C is the capacitance of EDLCs, ε is the permittivity of the insulating layer, S is the electrode area, and d is the distance between the electrodes. A difference is that in the case of two identical electrodes an EDLC can be considered as two capacitors serially connected through electrolyte and the total capacitance of the EDLC is

$$1/C=1/C_1 + 1/C_2, \quad (2)$$

And if $C_1 = C_2$, then

$$C = C_1/2 \quad (3)$$

According to (1), increasing specific area of electrodes leads to an increase of specific capacitance. As a result, developers give great consideration to materials for electrodes [2 - 4]. The criteria determining the suitability any material for electrode component in EDLCs are as follows: high specific inner surface, high conductivity, and its indifference with respect to electrolyte. Porous carbon materials [5, 6] and carbon nanotubes [7 - 9] best of all meet these criteria. There are many techniques for preparation of porous carbon materials not only due to various technological processes and their conditions but also because of available wide raw materials sources. Organic raw materials of vegetable nature are very promising for this purpose. Because of their variety, natural reproducibility, availability, cheapness, ecological purity the raw materials of vegetable nature have great attention for development of EDLCs [5, 8, 10 - 12].

I. Experimental

In this paper we investigate parameters of a porous carbon material, which was obtained from corn stigmas, an organic raw material of vegetable nature as well those of EDLCs with electrodes based on this material and a 6M aqueous solution of KOH as the electrolyte. The main technological details for obtaining the carbon material were described earlier in [13]. Operating samples of the EDLCs were manufactured in a dismountable cell with the area of each electrode equal to 2.7 cm^2 at the weight of the active carbon material equal 0.02 g. The electrodes were prepared by scattering the powdered material immediately on Ni foil electrode leads and then it was uniformly distributed over the surface. Two layers of an asbestos paper for chemical power sources (BAHIT-48) about of 48 μm thick were applied as the separator. Investigations of direct current (d.c.) characteristics of the EDLCs at their charging/discharging have been carried out by using a "SERIES 2000 BATTERY TEST SYSTEM" (MACCOR, USA). The impedance spectra were measured in the frequency range 0.01 to 10^5 Hz by means of a "Schlumberger 1255 H.F. Frequency Response Analyzer" coupled to a "Solartron 1286 Electrochemical Interface".

Taking into account that an electric double-layer capacitor consists, in fact, of two capacitors serially connected through the resistance of electrolyte, the specific capacitance of the material was determined from the relationship

$$C_S = \frac{2C_m}{m_1}, \qquad (4)$$

where C_S is the specific capacitance of a material, C_m is the capacitance measured at a discharge and m_1 is the mass of active material for one electrode. The discharge capacitance at a d.c. discharge was established from the technique described in [14], i.e. from the discharge curve part between 0.8 U_{max} and 0.4 U_{max}, where U_{max} is the maximum charge voltage. In the case of an aqueous alkali electrolyte U_{max} = 1 V.

II. Results and discussion

2.1. Investigation of the carbon material

Fig. 1 shows typical charge – discharge dependences obtained at d.c. conditions for samples of EDLCs with two identical electrodes. It is found that in the used charge – discharge cyclogram the EDLCs are not charged completely at a current density above 0.6 mA/cm^2. It follows from a voltage step ΔU at a charge-to-discharge transition. From values of ΔU an

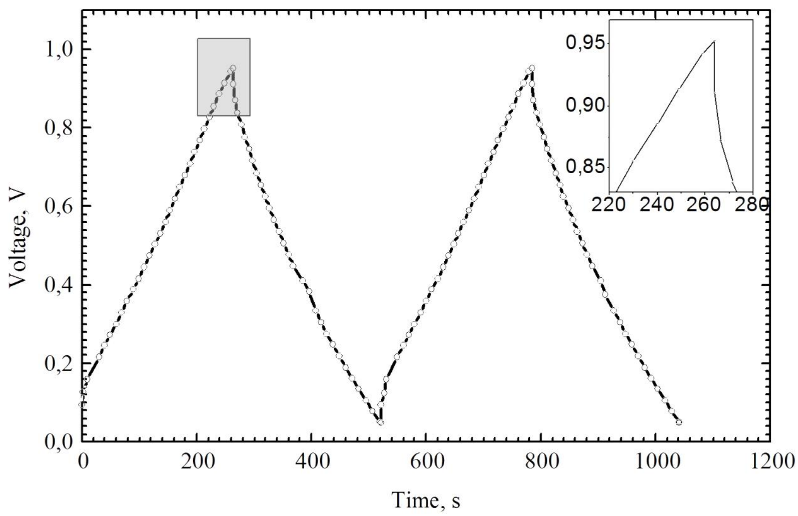

Fig. 1. A typical charge-discharge cyclogram for an EDLC in a d.c. mode

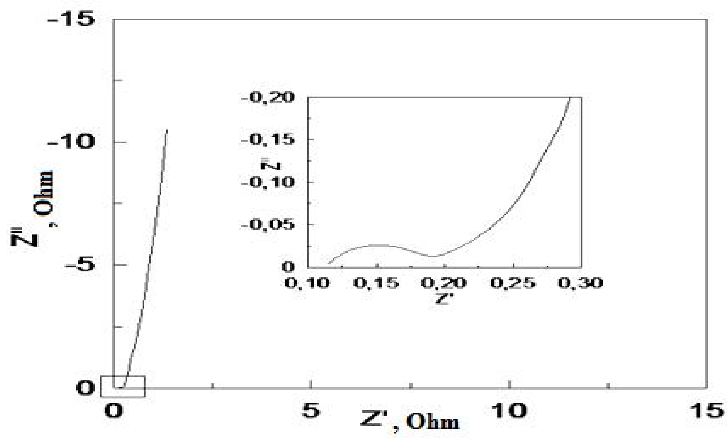

Fig. 2. A Nyquist plot for a 2325-sized EDLC

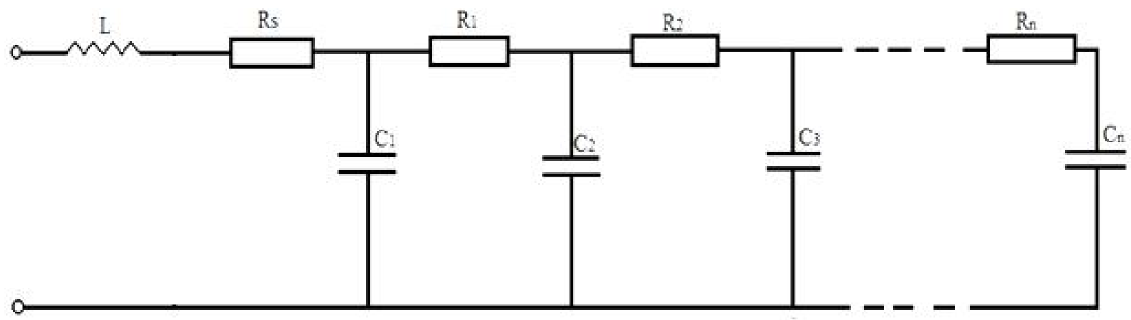

Fig. 3. A typical equivalent circuit for an EDLC with two identical electrdes based on the carbon material prepared from corn stigmas

estimation of the internal resistance ri of the EDLCs was carried out and in the case of undercharging the inaccuracy in determination of ri essentially increases. In order to minimize such errors at determination of parameters of the electrode material as well energy parameters of the EDLCs, it is necessary to carry out their two-step charge – a d.c. constant value charge followed by that at a direct voltage constant value. A time necessary to complete a charge is determined from a decrease of charge current density to values below 0.3 mA/cm^2.

Fig. 2 shows a typical Nyquist plot in the frequency range 10^{-2} to 10^5 Hz. As it is seen from the plot, a sample manufactured on the basis of two identical electrodes from our material and with a 6 M KOH aqueous solution as the electrolyte is a capacitor having low values of active resistance.

An equivalent circuit including elements characterizing the electrode – electrolyte interface was drawn starting from the impedance spectroscopy data. These elements describing processes at the interface were determined from a least-square fitting procedure by means of the Zview-2 software. The general view of the equivalent scheme is shown in Fig. 3. The elements of the scheme are as follows: RS – the series active resistance caused preferably by the electrolyte resistance as well the resistance due to the structural elements' resistance and possibly because of the resistance between the grains of the electrode material, L – the inductance depending on the structural elements of the sample, R1,C1…Rn, Cn – distributed resistances and capacitances because of porous structure of the electrode material.

At the Nyquist plot (Fig. 2) of the material under investigation one can distinguish three parts – high-, middle-, and low-frequency ranges. The high-frequency range has the form of an arc close to semicircle and corresponds to a parallel RC-circuit that describes charge transfer through the electrode–electrolyte interface. In most cases this resistance can be considered as an equivalent series resistance (ESR). The middle-frequency part has the form of a straight-line with a slope about of 45° to the abscissa axis and is caused by the distribution of resistances and capacitances in pores of the electrode material and diffusion processes (Warburg's range). So, on contrary to a normal capacitor, the EDLCs can be considered as a capacitor in which another resistance, named equivalent distributed resistance (EDR), is added to the usual ESR. The low-frequency part is a straight-line with a slope close to 90°. This part is caused by capacitance of the double electrical layer, i.e. a polarizability degree of the electrode. Some shift of the Nyquist plot to the right along the abscissa axis is caused by the series resistance of the electrolyte and the structural elements of the sample. As one can see, this Nyquist plot is typical for a capacitive system with porous electrodes. The determined specific capacitance of the electrode material determined from a d.c. discharge is equal 254 – 256 F/g. Being compared to the specific capacitances for 30 materials listed in Ref. [14], it is only inferior to a material MAXSORB (PX-21) with the specific capacitance of 322 F/g.

2.2. Investigation of experimental samples of electric double-layer capacitors.

On the basis of the obtained carbon material we have manufactured EDLCs of prismatic type with an aqueous (6M KOH) electrolyte. Perforated nickel plates (Ni NP-2) with the electrode material pressed on them were used as electrodes. The area of the plates was 95×95 mm^2, and the electrodes' thickness was about of 1 mm. The total amount of the plates was equal to 6 and the total area of the electrodes was about of 300 cm^2. Two layers of BAHIT-48 about were applied as the separator. It follows from the investigation that a d.c. capacitance of these EDLCs is 920 F at the maximum charge voltage 1 V. The capacitance was determined at a discharge current density $j_d \approx 0.01$ A/cm^2.with respect to the elecrode's area, i.e. at a total current $I_d = 3$ A. Starting from the impedance spectra measurements an equivalent circuit of the EDLCs was proposed and numerical values of its elements were determined. The maximum current obtained at a discharge through an external load $R_L = 0.006$ Ohm was 83 A.

Electric double-layer capacitors of a coin-type (2325 in size) were also investigated. The electrodes for them were prepared embedding a dose of the active carbon material (≈ 0.17 g) into a Ni grid. Their area was about of 2.8 cm^2 and the thickness was ≈ 0.95 mm. Such EDLCs have the average capacitance 10.6 F at an internal resistance 0.06 to 0.07 Ohm that corresponds to a specific internal resistance 0.21 to 0.25 Ohm·cm^{-2} with respect to the electrode area.

Conclusions

From the carried out investigations one can conclude that porous carbon materials prepared by pyrolysis of organic raw materials of vegetable nature and subjected to an appropriate subsequent activation procedure may be used as high-effective electrode materials for EDLCs with an aqueous electrolyte. Previous investigations of such materials indicate on opportunity for them to be used in EDLCs with electrolytes based on organic aprotic solutions. Starting from the specific energy - capacitance parameters of the obtained carbon material one can suppose about the existence of nanostructure inclusions in it caused by the natural structure of the initial vegetable raw materials.

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