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The Effects Accompanying Passing Current Through a Granular Bed of Activated Carbon

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Abstract. Repeatedly passing current of high intensity (2 A) in the pulsing mode through a granular bed of activated carbon was accompanied by changes of bed resistance. These changes did not diminish when the current stopped but proceeded during 2 to 10 days of exposure.

X-ray lattice parameters of the carbon before and after it was subjected to numerous current pulses have been measured. The second sample differed considerably because it was more amorphous. Nitrogen and water adsorption isotherms on these samples have been measured. They showed a reduction of specific surface area (volume of micropores) and probably an increase of the average diameter of mesopores.

The observed significant changes of carbon texture and structure are explained by inductive electromechanical interactions between planar layers of carbon atoms in microcrystallites of activated carbon during pulses of passing current.

Keywords: activated carbon, characterization of properties, regeneration

Introduction

Electroconductive properties of activated carbons are controlled by a great body of factors (microstructure, surface conditions, raw materials, production process, etc.). The literature (Khrenkova and Kasatochkin, 1969; Shulepov, 1972; Hernandez et al., 1982; Emmerich et al., 1987; Radeke et al., 1991; Bourrat, 1993) is not very useful for forecasting such properties.

In previous work (Alekhina, 1993) we have shown that electrical resistance determined by the current intensity no stronger than 0.001 A varies within the limits of two orders in different batches of the same activated carbon. We have tried to find a correlation between electrical resistance and activated carbons properties, as which have considered grain size, mechanical strength, mass density, ash content, pH of water extracts, content of surface acid groups, and X-ray characteristics (interplanar spacing, height of bundle layers, and crystallite length). Despite beginning with carbons of the same type, changes of properties tool place, but with one set we observed variations in resistance that did not correlate with the others.

From adsorption isotherms of nitrogen (77 K) and water vapor (298 K) we determined the structural characteristics of carbons: specific area, parameters of Dubinin's equation (Dubinin, 1966), total porosity, volume of micropores and total volume of macro- and mesopores. Resistance changes correlated only with variations of total volume of macro- and mesopores: when these increased, the resistance decreased.

We have assumed that the existence this correlation is connected to inductive interaction between current-carrying structural elements of activated carbon. The increase of total volume of macro- and mesopores corresponds to an increase of distance between current-carrying elements that apparently was accompanied by a reduction of inductive component of impedance and resistance as a whole. At present this explanation is not quite satisfactory to us and we continue research in this

direction. But the facts remain. They are the basis for our observations described in the present article. As the induction interaction has an electrical and mechanical nature, it should result in changes of a structure and texture of activated carbon. These are the changes we hoped to explain.

Experimental

Materials

We used high-quality Russian peat-based carbon that was activated using potassium sulfide (designated SKT). All samples were extracted from the same commercial batch. The complete structural description is presented elsewhere (Kolyshkin and Mikhailova, 1972).

Procedures

Samples were dried at 200°C in nitrogen, and placed in a cylindrical glass vessel of 6 cm in diameter. One of the electrodes was at the bottom, and the second electrode was laid over the granular bed, which was 7 cm in height. Both electrodes were made of stainless steel. The bed was compacted with an electrovibrator before measurement. Afterwards, a load of a certain mass was placed on the upper electrode to improve compaction and to stabilize its electrical characteristics. The specific static load was selected in preliminary experiments and constituted 50 g/cm^2.

During the experiments, a constant current was delivered to the electrodes in a pulse mode. Its intensity constituted 2 A, with a pulse duration of 1–2 s. Such a combination of parameters avoided significant warming-up of the carbon bed. As a result, the increase of temperature did not exceed 2 to 3 K. The sequence of consecutive pulses was administered during repeated intervals of 10–15 min, during which the carbon was unloaded from the vessel, re-loaded, then recompacted. Thus, in each experiment we used a "fresh" layer and grains with accumulated changes.

Resistance Measurements

The resistance of the activated carbon granular bed was measured before (R_b), during (R) and after (R_a) passing current. The resistance R was calculated from ratio $R = U/I$, where U = voltage drop in bed, V; and $I = 2$ A = current intensity. Measurements of the resistances R_b and R_a were conducted with use an ohmmeter at a current of about 0.001 A. The accuracy of these measurements was ±5%.

The resistances of the carbon grains (1.7 × 4 mm size) were measured with a milliohmmeter by placing them in spring-loaded clips of this device. Before measuring, the adsorbent grains were dried at 200°C in nitrogen. The resulting resistance was found as the average of 20 grains resistance. The overall measurement error was ±5%.

Measurement of X-Rayograms and Adsorptions Isotherms

These measurements were executed at the Institute of Physical Chemistry (Russian Academy of Sciences, Moscow). A DRON-3M diffractometer (irradiation $Cu_{K\alpha}$, Ni-filter) was used to measure X-rayograms. The isotherms were determined by a McBain vacuum balance. Prior to measurements, the samples were evacuated at 673 K and 1 mPa for 5 hrs.

Results

Changes of Resistance of Activated Carbon Granular Bed

The dependence of the measured resistances on pulse number is shown in Fig. 1. It is seen that $R \ll R_a < R_b$. That is, during and after passing current, the resistance of carbon is quite different from one before the pulses begin. The resistance shows a trend towards stabilization (but with some noise as the pulses proceed.

The carbon sample was left in the reactor for about 90 pulses. Afterwards, current was stopped, and the bed resistance (R_x) was determined at unequal intervals. The time dependence of bed resistance is given in Fig. 2, curve 1. At first this curve has a very sporadic, but after 10 days the resistance becomes quite stable.

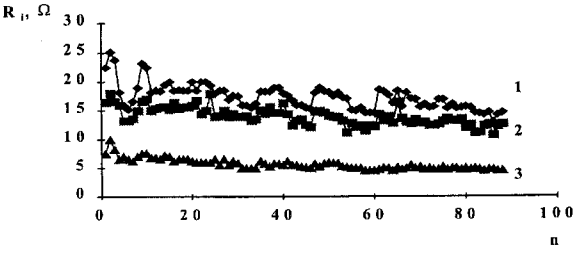

Figure 1. Dependencies of resistances R_i of activated carbon (SKT) bed on the number of current pulses n: (1) $R_b = R_b(n)$, (2) $R_a = R_a(n)$, (3) $R = R(n)$.

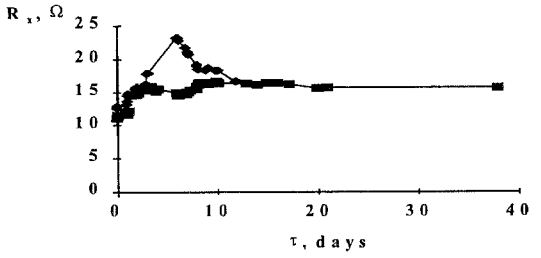

Figure 2. Relations between resistances R_x of activated carbon (SKT) bed and exposure time τ: 1—after passing the first pulse series. 2—after passing the second pulse series.

This stabilized carbon sample was again subjected to current pulses. In the second series R_b, R_a and R values were more stable and lower than ones in the first series. Curve 2 in Fig. 2 shows the change of carbon bed resistance after the second series of current pulses. Some sections of curves 1 and 2 are qualitatively similar: there are step increases in resistance at first, but after 2 days R_x on curve 2 becomes nearly stable.

It is known that activated carbon in an organic semiconductor with mainly electron conductivity. So great differences between R_b and R might be the reflection of this general feature of semiconductors. The number of free electrons in semiconductors is controlled by the applied voltage. But it seems that differences in R_b and R_a value should have another nature. We believed that, when passing current through the tested carbon, its structure and/or texture changed. This can be confirmed by the shapes of the curves in Fig. 2. These curves reflect slow changes, and such changes are reasonable to explain relaxation effects of a mechanical nature, not an electronic one.

X-Ray and Adsorption Measurements

Two carbon samples were selected for subsequent tests: the original material and a sample after 2 series of current pulses and double exposure. The second sample, i.e., the stabilized one, corresponds to the last point of curve 2 in Fig. 2.

Resistances of the carbon bed and individual grains were compared for these two samples. The results of this comparison are given in Table 1. As is seen from the table, the ratio of the bed resistances is approximately equal to the ratio of the grain resistance. So we can believe that the relationships observed in our carbon beds correspond to phenomena primarily in grains.

X-ray parameters of tested samples are given in Table 1. These data indicate that repeated current passage and exposure do not lead to changes in height of the bundle layers or crystallite size. But the interplanar spacing (d_{002}) and ratio I_{002}/I_b, where I_{002} and I_b are intensities of interference maximum (002) and diffusion background, respectively, vary to a substantial extent. The ratio is usually considered as a measure of order in tested materials (Shwartzman et al., 1986).

The adsorption isotherms of nitrogen (77 K) on the initial sample (curve 1) and stabilized one (curve 2) are indicated in Fig. 3. Specific surface areas calculated by the BET equation were 1550 and 1210 m^2/g, respectively.

The adsorption isotherms of water vapor are compared in Fig. 4. As is evident, there is a shift of the curve for the stabilized sample to the right, in relation to the initial sample's curve. This fact indicates that current pulses affect the sample results in two ways: a reduction of primary water adsorption centers (Vartapetyan, 1995) and a small increase in the diameter of mesopores. The former is a consequence of surface reduction or the concentration of oxygen-containing centers. The total porosity in the carbons structure, as follows from practical concurrence of values of water vapor adsorption at $P/Ps \sim 1$, probably, remains constant.

Table 1. Electric resistance and X-ray lattice parameters of carbon samples.

Sample	Resistance (Ω) bed*	Resistance (Ω) grain**	Interplanar spacing d_{002} (nm)	Height of layers bundle L_c (nm)	Crystallite length L_a (nm)	I_{002}/I_b
Initial	24.1	0.4	0.364	0.98	3.30	0.55
Stabilized	15.8	0.3	0.403	0.98	3.30	0.28

*Bed height 7 cm, diameter 6 cm.

**The average resistance of the grains were measured after drying up at 200°C in nitrogen.

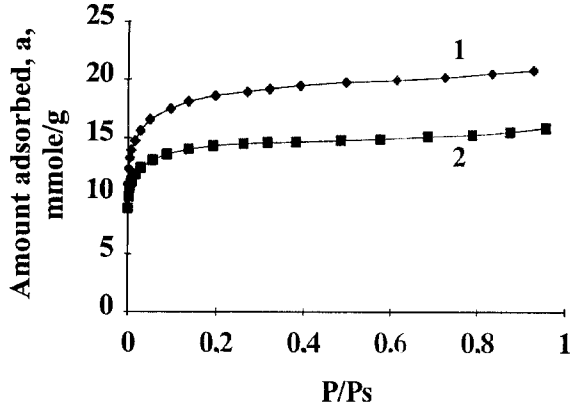

Figure 3. Adsorption isotherms of nitrogen on activated carbon at 77 K: (1) initial sample, (2) stabilized sample.

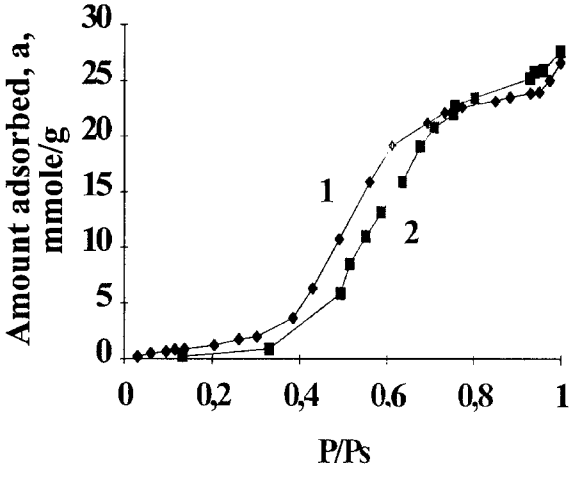

Figure 4. Adsorption isotherms of water vapor on activated carbon at 293 K: (1) initial sample, (2) stabilized sample.

Discussion

The data of the X-ray analysis and adsorption measurements, though different in terms, basically leads to the same conclusion: current passage is accompanied by partial loss of a crystallinity, resulting in increasing amorphousness of the sample. This result, as it is represented, can be explained by electromechanical interaction between conducting structures of activated carbon.

Conductivity of carbons, being graphite bodies, is realized principally by π-electrons along planes of hexagonal rings. Planar layers of carbon atoms in microcrystals of activated carbon can be considered as parallel conductors with current passing along them. Passage of current pulses effects the shift of layers because of inductive interaction between these conductors when a pulse passes. But there is a shift relaxation after passing. These displacements of layers, relative to each other, in other word, crystallite lattice modes, cause lattice disordering in a gradual manner. The disordering shows itself in the larger interplanar spacing of the crystallites and in lesser crystallinity. With passing pulses in carbon grains there might be displacements and reorientations in positions of some microcrystallites.

Activated carbon can be considered as a very complicated system, and its resistance is the result of many different factors. For instance, the higher the degree of amorphousness, the larger is the electrical resistance (Emmerich et al., 1987). An increase in distance between conducting elements causes a decrease of the inductive component of impedance and resistance itself. When amorphousness and interlayer distance increase simultaneously, the total effect might have various signs. The whimsical curves shown in Fig. 2 could be explained by these reasons.

Thus, the appearance of inductive electromechanical interaction in activated carbons, through which passes an electrical current seems to be rather probable. It is displayed between planar layers of carbon atoms in microcrystals of activated carbon and results in changes of both the texture and structure of carbon, as well as its adsorption properties and electrical resistance.

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