ON THE RELATION BETWEEN TEXTURE PARAMETERS
AND DOUBLE LAYER CAPACITANCE OF ACTIVATED CARBONS

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ABSTRACT

The porous textures of activated carbons and their electrochemical double layer capacitance (DLC) in organic electrolyte, prepared on the basis of spent coffee waste ground, were investigated by using low-temperature nitrogen adsorption and constant electric current cycling methods. A relation between texture parameters and DLC of activated carbon samples based on a modified H. Shi's model was established. On the basis of the experimental data the modified model was examined and the main parameters of the relation (DLC per unit of internal (C_{INT}) and per unit external surface area (C_{EXT})) were calculated. The possibility of linear relationship between the double layer capacity and specific (BET) surface area was discussed.

Keywords: activated carbons, texture parameters, double layer capacitance, specific surface area.

INTRODUCTION

Porous carbonaceous materials and especially activated carbons have been object of a great interest due to their various industrial applications. The increased need of high power energy storage systems has intensified the researches on these materials due to their advantages in the construction of supercapacitor systems [1, 2].

It is well known that activated carbons with high specific surface area could be also characterized with high specific capacity. A relation between these two materials characteristics was established theoretically [3]. However, what concerns the detailed quantitative description of this relation, especially the influence of different type texture parameters on the capacitance, the situation is still unclear. The use of different synthesis methods (including the type of precursor materials) and different treatment conditions lead to preparation of activated carbons with different morphological characteristics, hence, with different porosity structure and specific surface area. To this effect, a linear dependence between the general specific surface area and the double layer capacitance of activated carbons is rare and can be regarded as a result of interaction of the different texture components on the specific surface area, which is an integral parameter including many components, e.g. internal and external surface area.

Since the power density is strongly dependent on the porous texture of the activated carbons, as the porous texture directly controls quick accessibility to the store energy on the interface [4]. This fact shows the influence of the type and the character of the pores as

well as their size distribution on the electrochemical characteristics of activated carbon materials.

Since for a certain type of electrolyte, the specific capacity of the activated carbons as electrode materials in supercapacitors depends not only on the BET-area, but on the complex interference of the porous texture parameters. To the above mentioned morphological complex should be added also type of electrolyte, since in the case of inorganic electrolytes, the chemical nature of the carbon surface plays an active role [5].

In the flow of these considerations the model proposed by H. Shi [4] for describing the capacitance (C) – texture parameters relation for activated carbon materials is acceptable and useful for the explanation of the electrochemical behavior of those materials on the basis of the results of the conventional gas adsorption method only. Moreover, the concept of the double layer capacitance, composed of different contributions dependant on the surface texture parameter (external surface area) and the parameter representative for the micropore texture (micropore surface area), is more rational in comparison with the traditionally accepted approach to the specific capacitance related to the specific surface area of the activated carbons.

For the case of inorganic electrolyte Centeno and Stoekli [5] proposed alternative to Shi's approach, which appears that the variation of the capacitance value of activated carbon samples at high current densities depends essentially on the CO_2 –generating surface groups (mostly acidic) and on $1/L_0$ (the inverse of the average micropore width). However, the experimental data show that for activated carbons with low oxygen contents, the influence of is perceptible to the electrical double layer capacitance, and a direct relation between C and is difficult to be obtained in an apparent way, hence the H. Shi's approach seems to be more convenient.

For non-aqueous electrolyte, the use of the equation of H. Shi [4] is favorable, since the negligible or even missing role of the surface oxygen groups. The problem in this case is to evaluate to what extent the texture parameters included in the Shi's equation are optimal. The texturial parameter A_{MI}, m^2/g, (the surface area of the micropore walls where micropores being locally slit shaped) is defined, through the simple geometrical relation [6,7]:

$$W_0 = x_0 . A_{MI} \qquad (1)$$

where W_0, cm^3/g, is micropore volume and x_0 is half-width of the micropore size distribution curve maximum.

The term external surface area (A_{EXT}) does not obey to a strong definition. In many cases, there is not a clear distinction between the internal (A_{INT}) and external (A_{EXT}) surface area. The most appropriate for the present case is the definition given by Centeno and Stoekli [5,8]. According to them, A_{EXT} is the surface area (a found) in larger pores or outside of the carbon [5].

The internal surface will comprise the walls of all cracks, pores and cavities which are deeper than they are wide, while the external surface may be taken to include all the prominences and all of those cracks and pores which are wider than they are deep.

From this regard, in the general case mesopore surface area (A_{MES}) could not be identified as equivalent to A_{EXT} [4].

The value of A_{EXT} can be obtained from the comparison of the adsorption isotherm (nitrogen adsorption at 77 K) with a reference isotherms (as de Boer's t- plot and Sing's α_S – plot [9], or $n(C_{BET})$ – plots of Lecloux [10]).

A variant of the comparative method is the so called t/F method of Kadlec-Dubinin [11] which adapts the above mentioned method of de Boer's t- plot (describing non-porous systems) to micro-meso porous activated carbon materials. The t/F method is very convenient for the simultaneous distinction of the adsorption in the micropores from that on the mesopore surface. The results obtained by the t/F method for A_{MES} differ from those, calculated by reference isotherms for the same micro-meso porous activated carbons. Due to the base assumptions of the t/F method [11, 12] as well as the limitation of the values for the t-plot calculations (accepted limit of relative pressure, $P/P_0 \leq 0.34$), the obtained A_{MES} tend to correspond to the above mentioned A_{INT}, not to the A_{EXT}.

Undoubtedly, it is not possible to distinguish the part of the mesopores which contributes to A_{INT} from this contributing to A_{EXT}. With some approximation, one may assume that the part of mesopores simultaneously accounted by the t/F and α_S -, t- or $n(C_{BET})$ – plots, is negligible and will not have appreciable influence on further calculations.

In our opinion, the main part of A_{INT} is A_{MI}, which leads to the equation:

$$A_{INT} = A_{MI} + A_{MES} \qquad (2)$$

In this case, the equation of H. Shi could be modified as follows:

$$C = C_{EXT}.A_{EXT} + C_{INT}A_{INT} \quad or$$

$$\frac{C}{A_{EXT}} = C_{EXT} + C_{INT}\frac{A_{INT}}{A_{EXT}} \qquad (3)$$

For validation of the modified variant of the Shi's equation (eq.3) for the case of capacitance of activated carbons in non-aqueous electrolyte, it is necessary to synthesize activated carbons from the same genesis group, i.e. from identical precursor and by the same synthesis method. Such carbons will have identical morphology and chemical surface nature. Another requirement to these carbons is that they should show monotonic change of the surface parameters as well as of the porous texture parameters. The precise determination of surface and texture parameters however is needed in order to refine on their relationship.

The aim of the present study is the preparation and characterization of activated carbons obtained from spent coffee grounds and testing the applicability of the modified Shi's equation to the case of double layer electrochemical capacitors with non-aqueous electrolyts.

EXPERIMENTAL

Materials

Activated carbon materials, obtained by chemical activation with KOH of spent coffee grounds (Robusta species) were used for the purpose of the present study. Before the activation the spent coffee ground was treated at 573 K, in air for 4 hours and after that the carbonaceous material was ground to the particle size less than 600 mkm as a small part of the material was ground to the particle size less than 400 mkm.

The as obtained materials were mixed with granular KOH in a ratios 1:1 and 1:1.2 and ground into a gel-like solid using a mortar and pestle. The activation of the mixtures was carried out for 90 min under argon flow of 15 dm³/h at 943 K, 983 K, 1023 K, 1073 K and 1223 K (only for the material with particle size less than 400 mkm) in a horizontal furnace. After activation, the obtained materials were washed with 10 % solution of HCl and distilled water and were dried at 383 K for 6 hours.

Both treatment temperature and impregnation ratio are included in the sample designation as in the following example: CACTR – T = 670, 710, 750, 800, 950 for 943, 983, 1023, 1073 and 1223 K; R= 10, 12 for 1:1 and 1:1.2 impregnation ratio.

Physicochemical characterization

The characterization of the surface and porous texture of the samples was carried out by adsorption of nitrogen (77.4 K) using a conventional volumetric apparatus. The nitrogen adsorption-desorption isotherms were used for determining the following parameters: the specific surface area A_{BET} (according to the BET equation); the total pore volume V_t (calculated from the nitrogen uptake at the relative pressure of 0.95); The specific surface area of the mesopores A_{MES} (according t/F method); the mesopore volume (determined by substracting the total micropore volume from the total pore volume); the mean pore radius (as the ratio of the double total volume and A_{BET}, assuming a cylindrical pore model); the mesopore size distribution determined according to the Pierce method (using the adsorption branch of the isotherms); the micropore size distribution parameters and the half-width of the distribution curve maximum , according to the Simplified equation [13].

The particle size distribution of activated carbons produced was determined using Shimadzu Centrifugal Particle Size Analyzer, Type SA-CP-2.

Electrochemical tests

The preparation of the electrodes with different activated carbons is described elsewhere [14]. The sandwich-type symmetric cells with carbon electrodes and a ceramic-mat separator used in the electrochemical tests were assembled in a dry box. Five different cells were produced with different activated carbons as electrodes using as electrolyte tetraethylammonium - propylene carbonate (Et₄NBF₄-PC). The electrodes were prepared from a mixture of 90 % activated carbon powder and

10% polytetrafluorethylene binder (Aldrich, 60% suspension in water) and pressed on Al discs (surface area 1.75 cm^2). Constant current charge-discharge cycling of the cells was conducting over voltage of 1.25-2.5 V at current loading up to 180 mA.g^{-1} at room temperature using a battery tester (IMD-10, BG).

RESULTS AND DISCUSSION

The normalized isotherms of N$_2$ adsorption at 77.4 K for activated carbons are presented in Fig.1. The mesopore size distribution of the same samples is shown in Fig. 2.

The main parameters of the porous texture of the samples under investigation calculated from the corresponding N$_2$ isotherms are given in Table 1.

The data in Table1 clearly demonstrate the simultaneous influence of the two main synthesis factors – the impregnation ratio and thermal treatment temperature. It is seen that both BET area (A_{BET}) and W_0 are maximized at thermal treatment temperature around 1073 K and impregnation ratio 1:1.2 (precursor : KOH). While the impregnation ratio is kept 1:1, the increase of thermal treatment temperature within the range 943 – 1023 K do not lead to significant increase of A_{BET}. Within the same temperature range the increase of W_0 is more pronounced. At the same time the correspond-
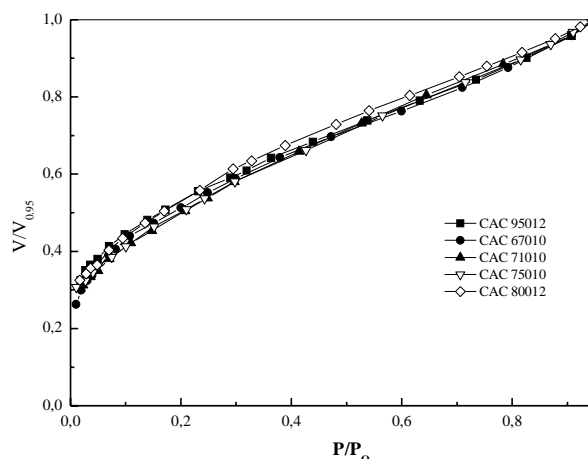

Fig. 1. Normalized nitrogen isotherms (77.4 K) on samples of activated carbons.

ing values of x_0 decrease, although the decrease is not sufficient to cause changes in the micro-meso porous character of the texture of the activated carbons.

At the impregnation ratio 1:1.2, the increase of thermal treatment temperature from 1073 K (CAC 80012) to 1173 K (CAC 95012) i.e. with 150°C, leads to a drastic decrease of A$_{BET}$ (~ 40 %) as well as of W$_O$ (~ 30 %) and to substancial increase of x$_O$ for CAC 95012 compared to CAC 80012 (with ~ 22 %) (Table 1). On the base of the change of W$_O$ and x$_O$ it may be concluded that as a result of the change of the chemical

Table1. Main surface and porous texture parameters of the activated carbons calculated on the basis of N$_2$ adsorption isotherms.

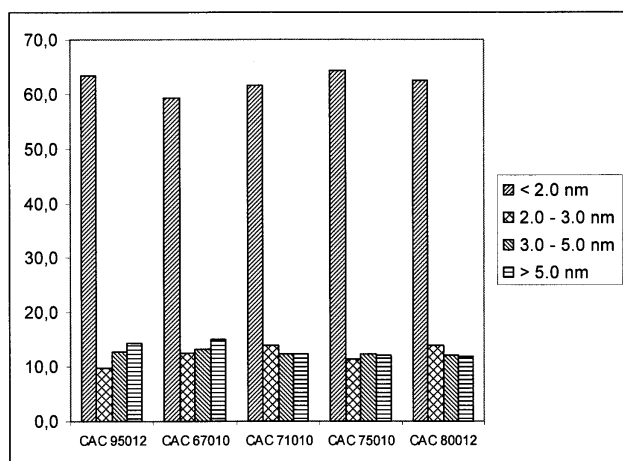| Samples	A_{INT}, m^2 g^{-1}	A_{EXT}, m^2 g^{-1}	A_{INT}, m^2 g^{-1}	A_{MES}, m^{2}g^{-1}	A_{MI}, m^{2}g^{-1}	V_t, m^3 g^{-1}	W_0, cm^3 g^{-1}	V_{MES}, cm^{3}g^{-1}	x_0, nm	R_p, nm
CAC 95012	689	37	338	59	279	0.555	0.262	0.293	0.94	1.6
CAC 67010	661	32	294	42	252	0.556	0.239	0.317	0.95	1.7
CAC 71010	706	34	341	37	304	0.605	0.277	0.328	0.91	1.7
CAC 75010	731	28	377	47	330	0.623	0.297	0.326	0.90	1.7
CAC 80012	1126	35	591	103	488	0.897	0.376	0.521	0.77	1.6

Fig. 2. Pore size distribution of the KOH activated carbons.

mechanism of the activation process [15] a change of the main parameters of the porous texture are observed.

From the Mesopore Size Distributions presented on Fig. 2 it is seen that the amount of mesopores ($R_p \geq$ 2 nm), which are very important when aprotic medium is used [16], vary between 36 and 41% of the sample total pore volume. This fact corresponds to the requirement for the amount of mesopores (between 20 and 50% of the total pore volume) of activated carbons used for supercapacitors [16].

It is apparent from the same figure that the values of the mesopores from the interval R_p: 2.0-3.0 nm, which have a very important role in ensuring the access of the ions on the aprotic medium used in the microporous texture of the activated carbon samples, are close. This value is lower only for the sample

CAC95012 with about 25% compared to the values of the other samples. (Fig. 2).

The prepared activated carbons (CAC 67010, CAC 71010, CAC 75010, CAC 80012) show a wide particle size distribution (from 40 to 180 mcm) with a maximum located at about 130 mcm. This means a partial disintegration of precursor particles occurs during activation under severe conditions of the study [17]. An exception is CAC 95012 sample, whose particle size distribution shows a relatively tight particle distribution (from 30 to 80 mcm) with a maximum at about 60mcm. Moreover, from the particular isotherm (Fig. 1) of the sample (in the region of capillary condensation - $P/P_0 \geq 0.35$) increased adsorbation is observed. It can be accounted by the presence of intra aggregate pores, i.e. with the tendency of the fine carbon particles of CAC 95012 to aggregate themselves, which is not inherent to the other carbon samples.

In Table 2 the measured capacitance values of the samples are shown and compared with the respective specific capacitances. From the data in Tables 1 and 2 it is apparent that the carbon samples show a tendency to increase their capacitance with the increase of A_{BET} and the porosity parameters (volume of the micro- and mesopores) as well as A_{INT}, which is related to them. It must be noted that the tendency of increasing the capacitance of the carbon samples is related with a decrease of x_0 parameter of the micropore size distributions. In this sense, the corresponding parameter acquires its lowest value for the sample CAC 80012 and, respectively, the highest capacitance (cf. Table

Table 2. Capacitance values of the activated carbons (according cyclic voltammetry) and specific capacitance, calculated per BET surface area of the samples.

Samples	Capacitance values (C), F/g	Specific capacitance (C_0), F/m^2	Δ^1, %
CAC 95012	17	0.0247	10.2
CAC 67010	18	0.0272	1.1
CAC 71010	20	0.0283	- 2.9
CAC 75010	21	0.0287	- 4.4
CAC 80012	32	0.0284	- 3.3

[1] $\Delta = \dfrac{\overline{C_0} - C_0}{\overline{C_0}} \cdot 100$, where $\overline{C_0}$ is the mean specific capacitance of the samples.
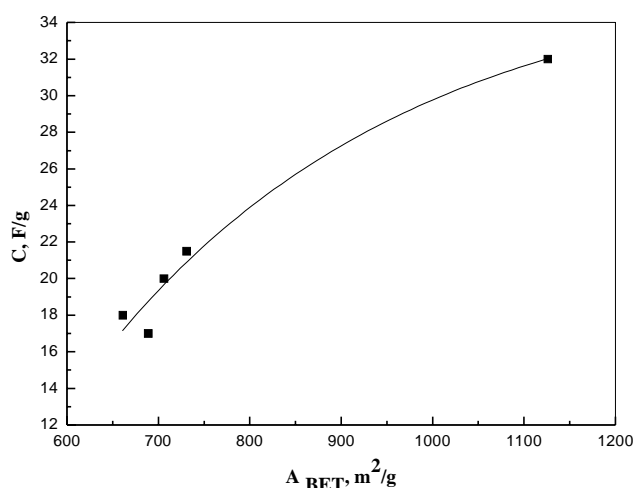
Fig. 3. Electric double-layer capacitance of the carbons samples (C) as a function of their BET specific surface areas (A_{BET}).

Fig. 4. $\dfrac{C}{A_{EXT}}$ plots as a function of $\dfrac{A_{INT}}{A_{EXT}}$ for activated carbons.

1 and 2). Simultaneously an increase in the volume of the mesopores is observed at practically constant values for the mean radius of the pores in all of the samples. In this case, the assumption that not the volume of the mesopores but the character of their size distribution determines the functions of the mesoporous texture seems to be valid. Fig. 3 shows the relationship between the capacitance and the specific surface area of the samples, determined by BET. Contrary to [16], for a linear relationship (for the case of A_{BET} <1000 m²/g), our experiments show that there is no direct proportional dependence between the BET surface area of the carbon and the capacitance measured.

When the values of the texture parameters in Table 1 are taken into consideration a possible explanation for the nonlinear relationship on Fig. 3 can be accepted to be that instead of using one fixed double layer capacitance for all sample porous surfaces [4], it is more reasonable to assume that the double layer capacitance per unit internal area (C_{INT}) is different from the capacitance per unit external area (C_{EXT}). On this basis, the capacitance (C) of the samples can be written (as mentioned above) as the addition of the two different parts:

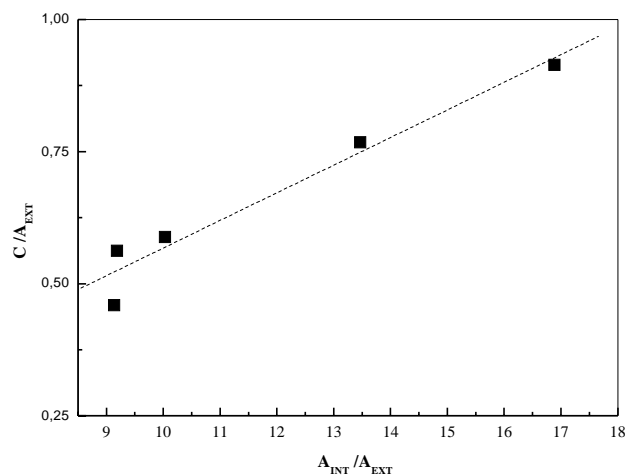$$\frac{C}{A_{EXT}} = C_{EXT} + C_{INT}\,\frac{A_{INT}}{A_{EXT}} \qquad (4)$$

The plots of $\dfrac{C}{A_{EXT}}$ vs $\dfrac{A_{INT}}{A_{EXT}}$

for different samples of activated carbons is shown in Fig. 4. From the linear fit (dashed line):

$$\frac{C}{A_{EXT}} = 0.0446 + 0.0523 \qquad (5)$$

the double layer capacitance per unit of different surface area can be estimated, correspondingly C_{EXT} = 0.0446 F/m² and C_{INT} = 0.0523 F/m².

The linear character of the relationship on Figure 4 probably will not convincingly prove that the external surface area has different electroadsorbtion behavior than the internal area when the double layer capacitance per unit area differs by about 15%. It is apparent that the mean specific capacitance $\overline{C_0}$ of the samples (0.0275 F/m²) is respectively 1.6 and 1.9 times lower compared to the values of C_{EXT} (0.0446 F/m²) and C_{INT} (0.0523 F/m²) calculated by Equation 3.

A possible explanation is that the electroadsorbation is carried out on the components of the specific surface (the specific surface, as defined by the Brunauer- Emet- Teller method, has an integral value) with different force.

Even with the samples synthesized by both the same precursor and method of activation, it is the method of preparation that determines the complicated mor-

phology of the external and internal [18] (micro- and mesopores) surface which leads to important changes of the double layer capacitance [4], specifically of the C_0 values on the specific surface area as a whole as compared to C_{INT} and C_{EXT} of the activated carbon samples.

CONCLUSIONS

On the basis of spent coffee ground activated carbons were synthesized with chemical (KOH) activation. The basic texture parameters of the carbons are determined by the low temperature adsorption of N_2 (77.4 K), while their electrochemical double layer capacitances in an organic electrolyte were obtained by the constant current charge - discharge cycling method. While maintaining the basic premise from the method proposed by H. Shi [4], the existence of a difference between the double layer capacitance per unit of micropore surface area and capacitance per unit of external surface area is assumed and a change of A_{MI} with A_{INT} (internal surface area), is proposed. The change is mathematically defined and does not introduce additional experimental complications in its calculation. On the basis of experimental data a linear relationship

$$\frac{C}{A_{EXT}} \text{ vs } \frac{A_{INT}}{A_{EXT}}$$

is obtained and C_{INT} (the capacitance per unit internal surface area) and C_{EXT} (the capacitance per unit external surface area) of activated carbon samples are calculated. The acquired values for C_{INT} and C_{EXT} are considerably higher than that of C_0 (specific capacitance per unit of BET surface area). The former may be accounted for by the resultant character of C_0 as a ratio of a sum of different capacitances per unit of constitutive parts of BET surface area, and the integral nature of surface parameter, A_{BET}.

Depending on the contributions of the capacitances per unit of the different constitutive parts (C_{INT}, C_{EXT}) of BET specific surface areas it may be possible or impossible to have a linear relationship between A_{BET} and double layer capacitance of the activated carbons.

The modified model suggested gives a possibility of optimization of texture parameters of the synthezied carbons in respect to their application as electrode materials for electrochemical double layer supercapacitors.

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