

CORRELATION OF THE CAPACITOR PERFORMANCE OF CARBON ELECTRODES WITH VARIOUS PARAMETERS OF ALKALI ACTIVATION

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INTRODUCTION

Activated carbons (ACs) are commercially available, cheap, and they can be produced with a developed specific surface area, depending on the activation (physical or chemical) parameters. ACs prepared by different procedures and from various precursors have been widely used for supercapacitor application (Qu, D. et al. 1998, Gambly, J. et al. 2001, Lozano-Castello, D. et al. 2003, Kierzek et al. 2004, Barbieri, O et al. 2005). It is well known that the specific capacitance of the electrode carbon material is described by formula (1):

$$C_{dl} = \varepsilon \cdot \frac{S}{d} \quad (1)$$

where C_{dl} is the double layer capacitance, S the surface area of the electrode/electrolyte interface, ε the permittivity of the electrolyte and d the thickness of the electrical double layer (of the order of 1 nm). Hence, we can expect that the higher the specific surface area of the carbon material, the higher the capacitance value. The general principle of an electrochemical capacitor is schematically represented in figure 1. The full capacitor is equivalent to two capacitors in series with capacitance values C_1 and C_2 for each electrode (positive and negative one). Formula (2) giving the overall capacitance C of the device demonstrates that the electrode with the smallest capacitance value decides about the total capacitance:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (2)$$

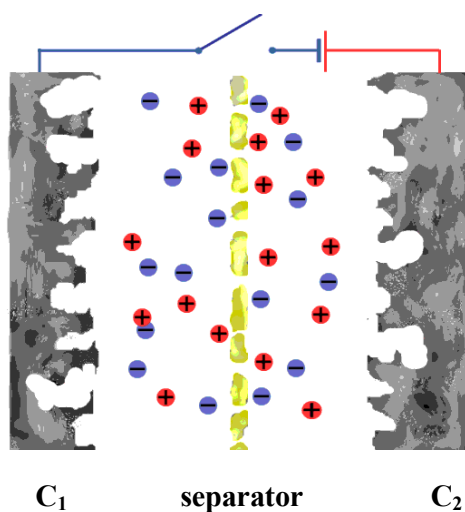


Figure 1. Principle of an electrochemical capacitor

The energy of the capacitor is given by formula (3) where U represents the voltage.

$$E = \frac{1}{2} CU^2 \quad (3)$$

As suggested by formula (1), the capacitance of ACs increases with their BET specific surface area, but without clear proportionality. A better proportionality has been found between capacitance and the amount of ultramicropores for various kinds of nanoporous carbons (Vix, C. et al. 2004, Chmiola, J. et al. 2006, Raymundo-Pinero, E. et al. 2006).

In the present work, the capacitance values as well as the capacitor performance will be correlated with the physicochemical properties of ACs obtained by various alkali activation procedures.

EXPERIMENTAL

Different carbon materials based on natural precursors A, B, C have been used for KOH and NaOH activation with various KOH and/or NaOH:C ratios (1:1, 2:1, 3:1, 4:1). Before the activation process, the materials were thermally pretreated. The activation was performed at different temperatures from 700 to 850°C with an activation time of half an hour. The resulting ACs were carefully washed out by diluted acid to remove the residual alkali. The BET specific surface area, the micro and mesopore volumes, as well as the pore size distribution of ACs were determined from nitrogen adsorption data at 77K using an ASAP 2010, Micromeritics. The t-plot method was applied to estimate the micropore volume and surface area.

The electrochemical characteristics of ACs were obtained in aqueous (1 mol.L⁻¹ sulfuric acid) and organic (1 mol.L⁻¹ tetraethyl ammonium tetra fluoroborate - TEABF₄) media by voltammetry, galvanostatic charge/discharge and impedance spectroscopy, using a multichannel potentiostat-galvanostat VMP-Biologic (France) and an AUTOLAB FRA2 (The Netherlands).

RESULTS AND DISCUSSION

The BET specific surface area and the micropore volume for all ACs are presented in Table 1. It clearly proves that KOH is more efficient for activation than NaOH. Comparing for example the material A-K1 for which the lowest KOH:C ratio 1:1 was used, with A-K4 (the ratio was 4:1), obviously demonstrates that the higher the ratio of KOH activating agent, the more developed the BET specific surface area. In the case of the precursor B, the specific surface area reaches a very high value of 3640 m²/g. Some trials performed with a mixture of the two activating agents show also a profitable effect on the surface area development.

Sample	BET [m ² /g]	V _{micro} [cm ³ /g]	S _{micro} [m ² /g]	C [F/g] acidic	C [F/cm ³] acidic	C [F/g] organic	C [F/cm ³] organic
A-K1	827	0.376	811	96	47	74	37
A-K2	1794	0.862	1760	139	54	114	45
A-K3	2421	1.267	2361	189	54	150	43
A-K4	2670	1.495	2614	219	62	150	42
A-Na2	712	0.314	655	80	48	87	52
A-Na4	1125	0.530	1051	121	66	115	63
A-K2Na2	2163	1.058	2097	183	80	123	54
A-K4T	2470	1.371	2421	175	50	117	33
B-K3	3483	1.686	3433	250	65	157	41
B-K4	3640	2.032	3562	250	64	196	50
C-K3	2440	1.141	2372	210	79	149	56
C-K4	2657	1.314	2556	199	69	168	59
C-Na4	1035	0.523	965	112	52	128	60
C-K2Na2	1747	0.887	1707	150	56	152	57
C-K4T	2329	1.190	2263	167	60	128	51
C-K3-700	1648	0.765	1601	216	83	123	47
C-K3-750	2331	1.071	2270	228	86	153	58
A/C-K3	2724	1.318	2666	214	64	146	44

Table 1 Physicochemical parameters and capacitance values for a series of alkali activated carbons (K stands for KOH activation and Na for NaOH activation). A, B and C means three different precursors. The capacitance values were calculated from the impedance spectra at 1 mHz

A few examples of nitrogen adsorption/desorption isotherms at 77 K are presented in Fig. 2. The shape of the curves clearly demonstrates for all the samples a highly microporous character together with a significant amount of mesopores. On the other hand, the lower ratio of activating agent 3:1 and the lower activation temperature of C-K3-700 are at the origin of the almost “pure” microporous character of the sample (the BET and microporous surface are almost the same, i.e., 1648 and 1601 m²/g, respectively).

The capacitance values reported in table 1 were measured in two-electrode swagelok cells, and they are expressed per mass of active material for one electrode, whereas the volumetric capacitance is related to the total volume of the electrode. Especially, high capacitance values (250 F/g) have been obtained in acidic electrolyte for the ACs B-K3 and B-K4 which exhibit the highest BET specific surface area. In organic solution, a value of 196 F/g was reached for B-K4. It is noteworthy that, due to a too extended development of porosity and a related low value of specific gravity, the volumetric capacity is not optimal for these samples. The best volumetric capacity was obtained for samples with a more moderate specific surface area, e.g., C-K3.

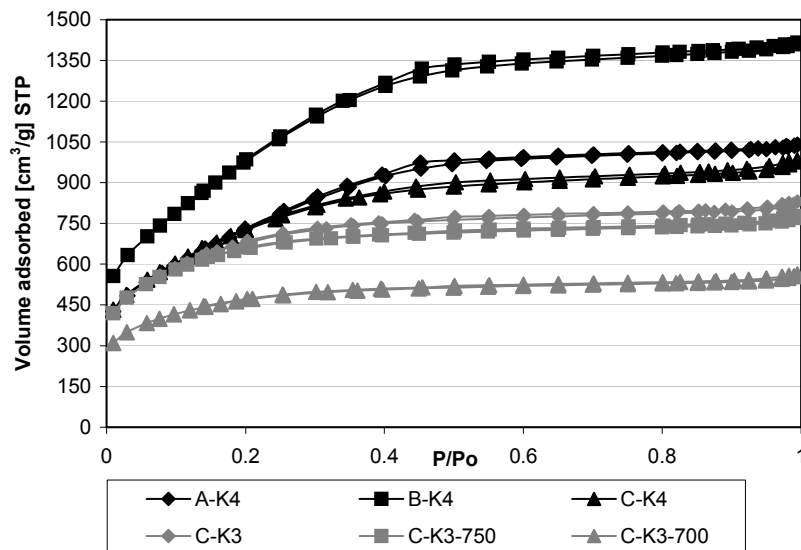


Figure 2. Nitrogen adsorption /desorption isotherms at 77 K on activated carbon materials A, B, C obtained with KOH activation using 4:1 and 3:1 ratio and different temperatures 850, 750 and 700°C.

Examples of voltammetry characteristics in organic medium are presented in Fig. 3. The heat treatment at 900°C of the two types of KOH activated carbons (4:1) has a positive effect on the capacitor characteristics. The operating voltage could be easily extended to 2.3 V, whereas only a range of 2 V was possible before thermal treatment. Obviously, heating first removes all the oxygen surface functional groups which are at the origin of the organic electrolyte decomposition and, additionally, it may moderately improve the conducting properties of carbon.

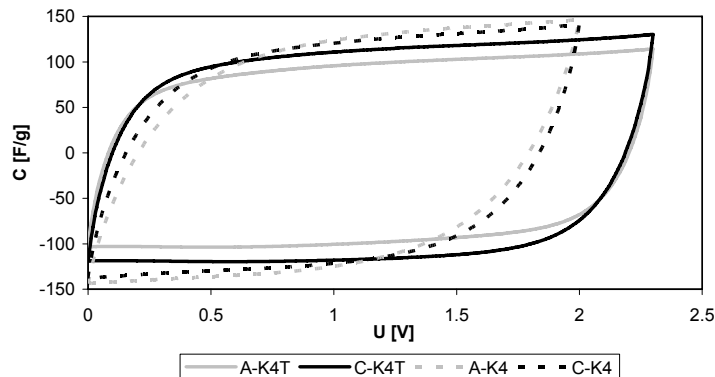


Figure 3. Cyclic voltammetry curves (100 mV/s) for two types of ACs prepared with the same KOH:C ratio 4:1 and further thermally treated at 900°C for 3h. Electrolyte : 1 mol.L⁻¹ TEABF₄ in acetonitrile.

The application of organic electrolyte gives lower values of capacitance (120-150 F/g), however, the operating voltage is greatly enhanced, that gives higher energy values reaching 30 Wh/kg.

Figure 4 shows the capacitance values from impedance spectroscopy measurements depending on frequency. Such a dependence gives a perfect view on the pores accessibility for ions, and in turn, the charge propagation. It seems that the 3:1 KOH:C ratio with an activation temperature of 750°C is sufficient for an optimal development of porosity (sample C-K3-750, acid medium). However, for a better charge propagation, a higher ratio 4:1 which supplies an additional mesoporosity is more convenient. Taking into account the cost of the total process, a lower ratio of activating agent could be envisaged.

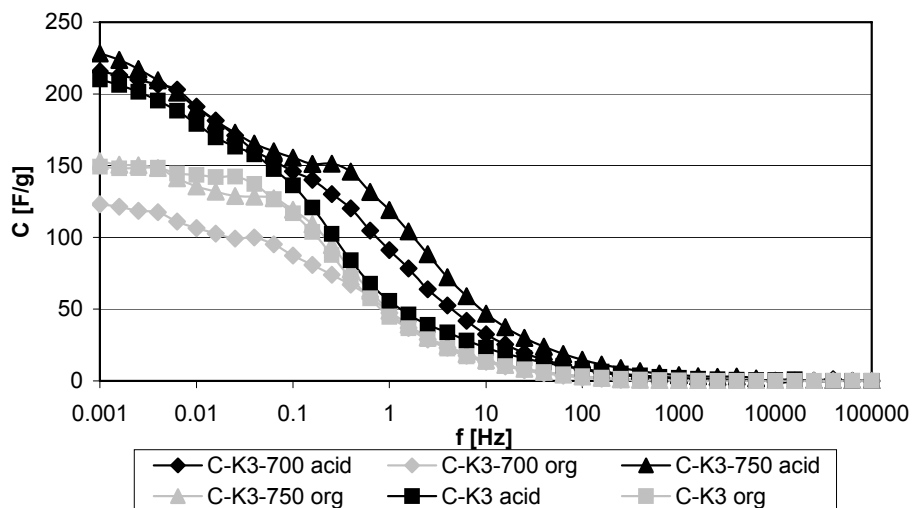


Figure 4. Capacitance vs frequency response in acidic and organic electrolytes for samples activated at different temperatures 700, 750 and 850°C

The values of capacitance versus the current load are presented in Fig. 5. It is noteworthy that values of ca. 60 F/g could be obtained at extremely heavy regime of 100 A/g for the sample A-K4 (with a KOH:C ratio equal to 4:1).

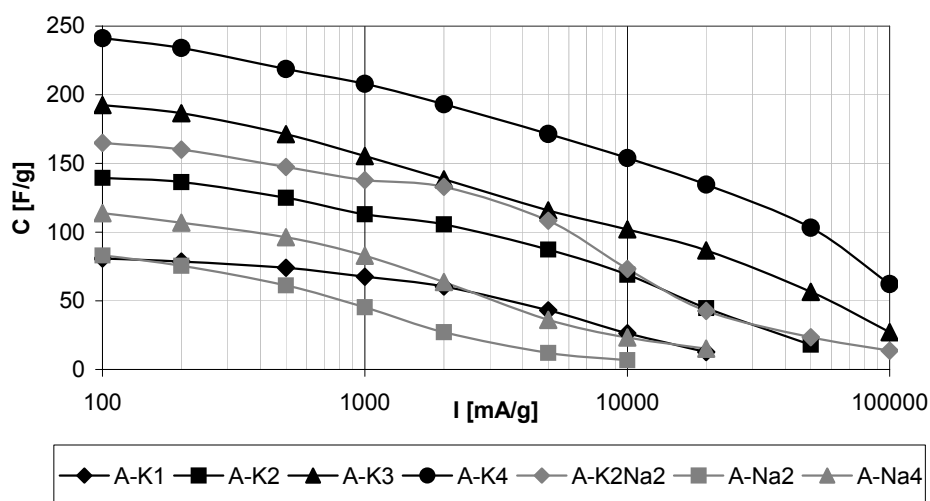


Figure 5. Capacitance values vs current load for samples activated at 850°C by KOH, NaOH and mixtures of alkalis at different alkali:C ratios. Electrolytic solution: 1 mol.L⁻¹ H₂SO₄.

Cycle life has been estimated for all the samples using galvanostatic charge/discharge at current loads of 500 mA/g and 1000 mA/g. The best cyclability was obtained for the sample C (10,000 cycles at 1A/g current load with only 10% loss of capacitance).

After analysis of all the data, it can be concluded that especially highly microporous carbons have been obtained from precursor B. It proves that the porosity development is a complex phenomenon which is affected by many parameters, such as the precursor composition and the activation parameters.

In the present work, only nitrogen adsorption was used for the estimation of microporosity. Carbon dioxide adsorption would be helpful to measure the exact amount of ultramicropores (pores below 0.7 nm). Indeed, it is well accepted that, for an optimal attraction of ions (lack of space charge) and the highest capacitance values, the pore size of ACs must fit well with the size of ions. A distortion of the solvation shells in pores below 1 nm was suggested that allows a close approach of the ion center to the electrode surface. However, for a high dynamic of charge propagation, some amount of small mesopores (below 2-3 nm) is necessary.

CONCLUSIONS

The following conclusions can be drawn from the present research:

- NaOH is less effective as activating agent than KOH for all the activated samples
- Mixture of two activators (NaOH and KOH) gives in some cases promising results
- KOH activation with ratio (KOH:C 3:1) seems to be optimal, however, for a higher charge propagation ratio 4:1 is also acceptable
- Further heat treatment (at 900°C) of ACs improves the capacitor performance, especially in organic medium; the voltage range can be easily extended from 2 V to 2.3 V with a good cyclability over 10,000 cycles
- Highly developed specific surface area (over 3500 m²/g) has been obtained in the case of AC type B, however, capacitance values in organic medium drop significantly from 196 F/g at 1 mHz to 90 F/g at 20 A/g current load.
- The volumetric specific capacitance reached the optimal values for microporous carbons but with a very low mesoporous amount.
- Activated carbons type C supplied high capacitance values, especially in organic medium, with a perfect cyclability at 1A/g current load. The energy values of 30 Wh/kg have been reached.

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