EFFECT OF PARTICLE SIZE ON THE CAPACITANCE PROPERTIES OF ACTIVATED CARBONS

G. Lota and E. Frackowiak, Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Piotrowo 3, 60-965 Poznan, Poland

INTRODUCTION

Activated carbons are still the most popular electrode materials for supercapacitor application. Important parameters of activated carbons affecting capacitance are: micropore volume, pore size and their distribution, micro/meso ratio, surface functionality. Conductivity is another very important parameter which is affected by particle size of material.
In the present work a special attention will be devoted to effect of particle size distribution of activated carbons which affects contact resistance between grains of material. Effect of particle size on capacitor performance will be analysed for a series of alkali activated carbons.

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 ratio (1:1, 2:1, 3:1, 4:1). Before activation process the materials were thermally pretreated. Activation process was performed in different temperatures from 700 to 850 ^{0}C. Time of activation was always half an hour. A careful washing of carbons was carried out by diluted acid to remove the residual alkali. Activated carbons were characterized in detail physicochemically to estimate BET specific surface area, micro and mesopore volume as well as pore size distribution. For adsorption of nitrogen at 77K an apparatus ASAP 2010 was used. T-plot method was used to estimate microporous volume and microporous surface area of activated carbons. A special attention has been devoted to measurements of particle size of activated materials. Particle size of activated samples was measured on apparatus Hydro 2000S(A).
Capacitance measurements were performed in aqueous (1M sulfuric acid) and organic (1M tetraethyl ammonium tetra fluoroborate $TEABF_4$) media by voltammetry, galvanostatic charge/discharge and impedance spectroscopy. Multichannel potentiostat-galvanostat VMP-Biologic, France and AUTOLAB FRA2, Netherlands have been applied for electrochemical investigations.

RESULTS AND DISCUSSION

Different activated carbon materials have been tested as capacitor electrodes in aqueous and organic electrolytic solutions. A special attention has been devoted to particle size of material obtained by alkali activation. A range of particle size of material used for activation was also controlled. Correlation of the particle size distribution and texture parameters of carbon with gravimetric but also volumetric capacitance was performed. Table 1 presents the capacitance values of three groups of activated carbons obtained from different precursors (A, B, C). The samples were obtained using various activation ratio as well as different activator. Fig. 1 presents dependence of % contribution vs different fractions of particle size for activated carbon type A prepared by KOH: (1:3 and 1:4 ratio) and NaOH (1:2 and 1:4 ratio) activation at 850^{0}C. Fig. 2 and 3 shows the the same dependence but for carbon sample B and C. Particle size distribution is strongly affected by precursor but also by activation parameters. More narrow particle size distribution with a smaller fraction from 10-50 μm can be found for a series A (Fig.1). One can say that using lower ratio of activator (3:1) and lower temperature of activation (700 – 750 C) results in smaller particles. In the case of carbon B a different ratio of activator does not affect significantly a particle size distribution (Fig. 2). Only a slight development of bigger particles is observed for 4:1 ratio.On the other hand, a significant shift to a big size of particles (ca. 200 μm) is observed for carbon C. Fig. 4 shows capacitance values versus % contribution of two fractions 10-50 and 50 to 100 μm for carbon A. This dependence clearly supports the conclusion that particles from 50 to 100 μm seem to be the best size. Quite good correlation of capacitance with this particle size is remarked (Fig. 4) whereas the contribution of smaller dimensions are not profitable.

Table 1. Capacitance values measured by impedance spectroscopy at 1 mHz for three types of carbons A, B, C prepared by different activation procedure and contribution of their different particle size fractions

Sample	C* [F/g] acidic	C* [F/g] organic	Fraction <10 μm [%]	Fraction 10-50 μm [%]	Fraction 50-100 μm [%]	Fraction 100-200 μm [%]	Fraction >200 μm [%]
A-K1	96	74	5.2	17.2	38.8	34.3	4.4
A-K2	139	114	25.0	49.1	21.6	4.3	0.0
A-K3	189	150	23.3	52.2	21.7	2.9	0.0
A-K4	219	150	11.6	32.9	34.8	19.3	1.4
A-Na2	80	87	28.1	57.4	13.0	1.5	0.0
A-Na4	121	115	23.4	53.7	18.9	3.9	0.0
A-K2Na2	183	123	25.8	41.6	22.8	9.1	0.7
A-K4T	175	117	14.7	47.0	28.3	9.5	0.4
B-K3	250	157	4.8	46.6	41.8	6.7	0.0
B-K4	250	196	4.9	41.0	42.8	11.4	0.0
C-K3	210	149	2.1	12.4	21.3	33.8	30.4
C-K4	199	168	2.3	13.9	32.3	32.4	19.1
C-Na4	112	128	1.0	2.5	10.6	38.5	47.3
C-K2Na2	150	152	0.7	1.5	7.1	38.7	51.9
C-K4T	167	128	2.2	14.3	26.2	32.9	24.5
C-K3-700	216	123	0.7	11.6	44.9	38.8	4.0
C-K3-750	228	153	0.6	10.6	44.6	39.4	4.8
A/C-K3	214	146	6.9	22.1	33.2	27.6	10.3

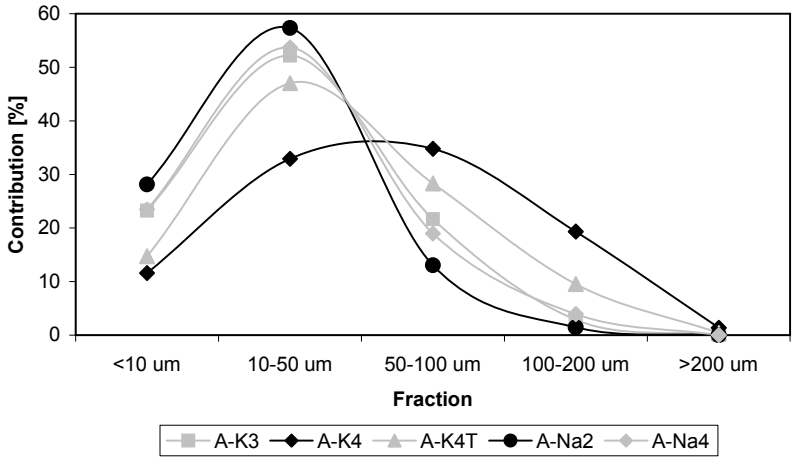

Figure 1. Dependence of % contribution vs different fractions of particle size for activated carbon type A prepared by alkali activation: KOH (1:3 and 1:4 ratio) and NaOH (1:2 and 1:4 ratio)

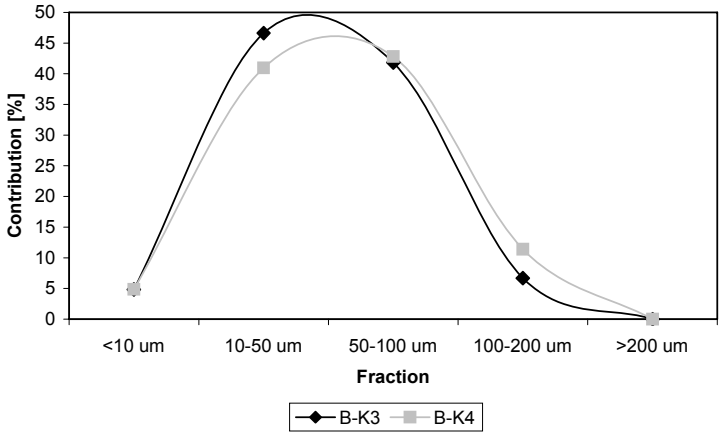

Figure 2. Dependence of % contribution vs different fractions of particle size for activated carbon type B prepared by KOH activation (1:3 and 1:4 ratio) at 850^0C

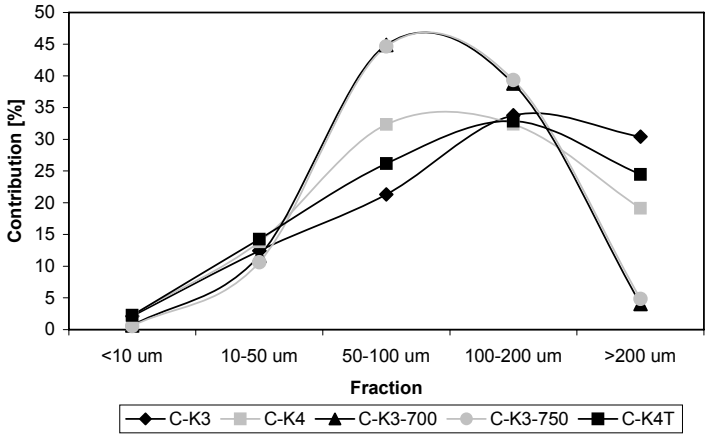

Figure 3. Dependence of % contribution vs different fractions of particle size for activated carbon type C prepared by KOH activation (1:3 and 1:4 ratio) at different temperatures 700^0C, 750^0C and 850^0C

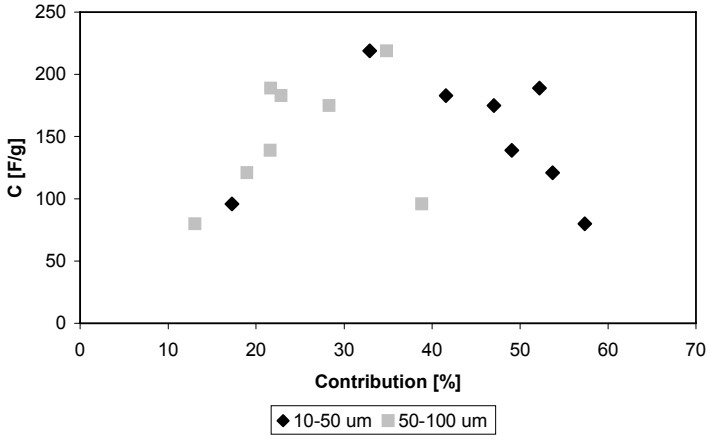

Figure 4. Dependence of capacitance vs contribution of two fractions of particle size for carbon type A. Acidic electrolyte – 1M H_2SO_4.

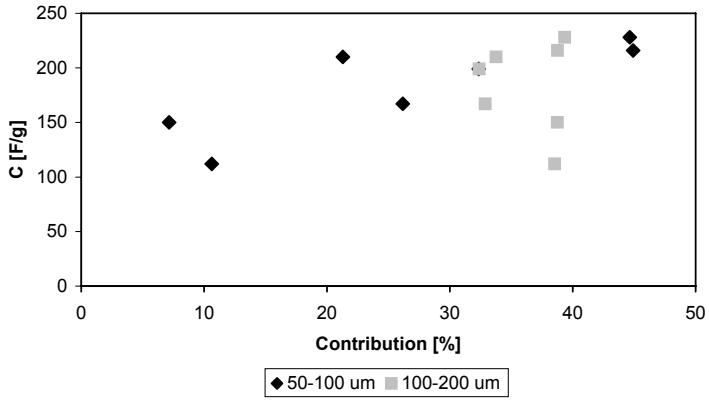

Figure 5. Dependence of capacitance vs contribution of two fractions of particle size for carbon type C. Acidic medium – 1M H_2SO_4.

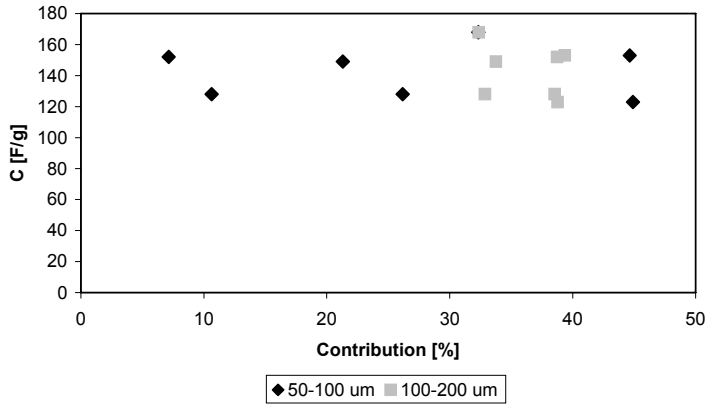

Figure 6. Dependence of capacitance vs contribution of two fractions of particle size for carbon type C. Organic medium.

Taking into account carbon type C which is characterized by a bigger range of particles size (from 50 to 200 μm), it is difficult to correlate capacitance values with contribution of two particle fractions. In acidic medium a great discrepancy is observed (Fig. 5) whereas in aprotic medium capacitance varies from 120 to 160 F/g being independent on fractions contribution (Fig. 6).

CONCLUSIONS

It can be concluded that capacitance values of electrode materials prepared by chemical activation are determined mainly by nanotextural parameters of carbon, mainly microporosity developed during activation. However, particle size distribution of material cannot be neglected because it decides about the conducting properties. The particle size distribution rather plays a secondary role on electrochemical properties. Obviously too small particles are not useful because of a significant increase of internal contact resistance between particles. On the other hand, too big particles are not convenient from technological point of view. In this case it is not easy to produce a homogeneous slurry, a well dispersed and flexible electrode material with a good adhesion to current collector.

It seems that optimal particle size belongs to range from 50 to 100 μm. It is rather difficult to draw the conclusions from all the investigated materials, however, considering separately subsequent groups of activated materials some clear tendency can be observed.