KOH ACTIVATED CARBONS FOR SUPERCAPACITORS

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Introduction

Electrochemical capacitors are power storage devices which performance is based on the charge accumulation from an electrolytic solution through electrostatic attraction by polarized electrodes. The capacitance of this system is directly proportional to the electrode surface, therefore carbons are very efficient for this application because of various possibilities of their modification and creation of a controlled pore size distribution [1-4]. The electrostatic attraction of ions takes place mainly in micropores, however, the presence of mesopores is necessary for an efficient charge propagation. It is noteworthy that the electrochemically active surface is not the same as the physically described surface area from nitrogen adsorption data, and is determined by the ability of ions to be trapped (size of ions, wettability, conductivity of carbon ..). Hence, in general a well-balanced micro/meso porosity is an important criterion for the selection of the carbon material.
In this presentation, we will pay a special attention to KOH activated carbons with a very developed porosity to study the role of surface area, size of pores, elemental composition on capacitor performance and cycleability.

Experimental

Natural precursors have been selected for KOH activation such as coal (C), coal semi-coke (CS), pitch semi-coke (PS) and pitch mesophase (PM). An industrial activated carbon (AC) was also used. Activation was performed at 800^0C by KOH with 4:1 (C:KOH) weight ratio for 5 hours followed by a careful washing of the samples with 10% HCl and distilled water. The activation process supplied highly microporous carbons with BET specific surface areas from 1900 to 3150 m^2/g. The BET surface area together with the micro and the total pores volumes of the KOH activated carbons are presented in Table 1. The mean micropore width calculated from the Dubinin equation is designed as L_D.
The capacitor electrodes were pellets formed by pressing a mixture of the active carbon material (85wt%) with a PVDF binder (10wt%) and acetylene black (5wt%). The capacitance measurements were performed in 1 mol l^{-1} H_2SO_4. The values of capacitance were estimated by voltammetry (scan rate of potential from 2 to 10 mV/s) and galvanostatic charge-discharge cycling (ARBIN BT2000, USA). Impedance

spectroscopy (AUTOLAB-ECOCHEMIE BV) allows the capacitance (F/g) dependence versus frequency (Hz), series resistance, time constant and charge propagation to be evaluated. For some samples a careful analysis of leakage current, self-discharge and capacitors cycleability was performed.

Results and Discussion

KOH activated carbons constitute an interesting class of capacitor electrodes due to their highly developed surface area of the order of 3000 m^2/g [5]. Especially, cheap natural precursors are well adapted for this process. The activation process is strongly affected by the C:KOH ratio, temperature and time. The optimal ratio seems to be 4:1 and the temperature for activation ca. 800 ^0C. The total activation process is quite complicated and proceeds via different pathways and by-products. The following reactions can be considered:

$$2KOH \rightarrow K_2O + H_2O \qquad (1)$$
$$C + H_2O \rightarrow CO + H_2 \qquad (2)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$
$$K_2O + H_2 \rightarrow 2K + H_2O \qquad (4)$$
$$K_2O + C \rightarrow 2K + CO \qquad (5)$$

Under severe conditions (above 700^0C), potassium vapour is formed that plays a special role in the activation of carbonaceous materials, easily penetrating in the graphitic domains which form cage-like micropores. The efficient development of micropores, which gives often a few-fold increase of the total specific surface area is very useful for the application of these materials in supercapacitors [4].
Table 1 shows the general porosity properties of KOH activated carbons used in our capacitor studies.

Sample	S_{BET} $m^2\ g^{-1}$	V_{DR} $cm^3\ g^{-1}$	V_{total} $cm^3\ g^{-1}$	L_D nm
A-C	3150	0.951	1.612	1.39
A-CS	3190	0.936	1.446	1.36
A-PM	2660	0.839	1.209	1.37
A-PS	2750	0.859	1.227	1.34
A-AC	1900	0.609	1.051	1.29

Table 1. Porosity parameters of the KOH activated carbons
(A-C means activated carbon from coal C etc.)

Our target is to correlate capacitance values with the total specific surface area, pore size distribution, particle size and elemental composition of carbon.
From three electrochemical techniques the most reliable capacitance results are obtained from galvanostatic discharge, however each method supplies complementary information. A typical galvanostatic charge-discharge characteristic for carbon A-PM is shown in Figure 1. The curve presents a correct triangular shape without a significant

ohmic drop. The values of specific capacitance per mass of carbon material and per surface area estimated by all three electrochemical methods using 1 mol l^{-1} sulfuric acid solution are given in Table 2. All the carbons present a very satisfactory capability of charge accumulation in the electrical double layer with capacitance values ca. 300 F/g, especially for the activated carbons from coal (A-C) and mesophase pitch (A-PM). The highest capacitance value for A-C well correlates with a maximum total pore volume of 1.6 cm^3/g and its BET surface area of 3150 m^2/g. However, a careful comparison of the carbons characteristics (Table 1) with the capacitance values (Table 2) shows that there is not a proportional relation between the surface area or the pore volume and the electrochemical behavior. On the other hand, from the low values of capacitance per surface area (7 to 11 $\mu F/cm^2$) one can assume that not all the micropores take part in the charge accumulation. It is clear that the micropores not adapted to the size of the solvated ions will not take part in the double layer charging. The charging of the double layer is very complex and depends also on other parameters such as the pore size distribution, the affinity to the electrolytic solution, the hydrophobic-hydrophilic character, the particles conductivity and their size.

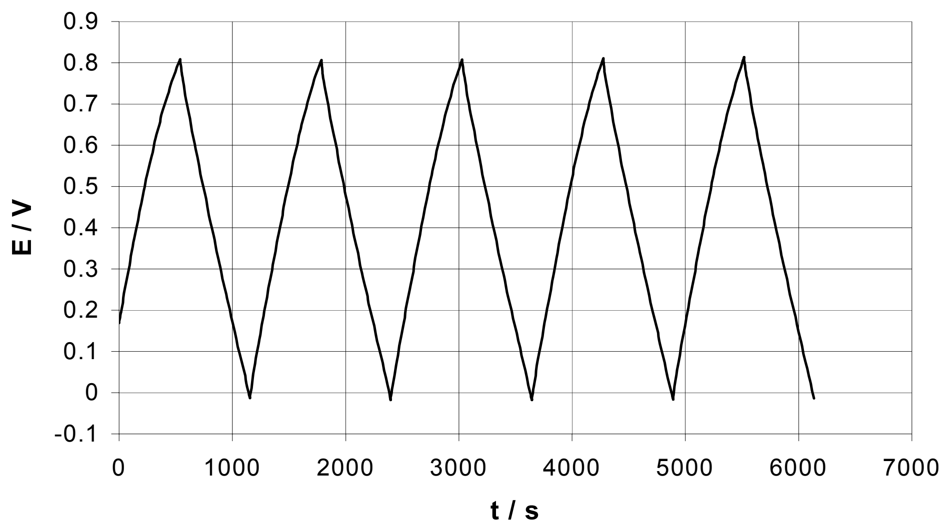

Figure 1. Galvanostatic charge/discharge characteristics of capacitor built from KOH activated carbon A-PM (mass of electrodes 12.2 mg/12.8 mg) I = 2 mA. Electrolytic solution 1mol l^{-1} H_2SO_4.

Even if the KOH activated carbons supply high capacitance values, the practical application of such materials is determined by the supercapacitor cycleability, a quick charge propagation at different loads, a low self-discharge. Highly microporous carbons supply always some diffusion limitation. This effect can be observed at quick scan rates during voltammetry experiments and during impedance spectroscopy measurements. Figure 2 shows the impedance characteristic for the carbon A-PM with almost perpendicular dependence of imaginary part to real one that is a proof for capacitive response, however, a small diffusion slope is slightly marked.

Sample	Galvanostatic discharge C / F g^{-1}	Cyclic voltammetry C / F g^{-1}	Impedance spectroscopy C / F g^{-1}	Specific capacitance μF cm^{-2}
A-C	312	317	282	9.9
A-CS	223	235	206	7.0
A-PM	294	299	273	11.0
A-PS	261	241	227	9.5
A-AC	198	198	193	10.4

Table 2. Capacitance values (F g^{-1}) of the KOH activated carbons (A-C; A-CS; A-PM; A-PS; A-AC) estimated by galvanostatic discharge, cyclic voltammetry and impedance spectroscopy. Specific capacitance μF cm^{-2} calculated per surface area of carbon

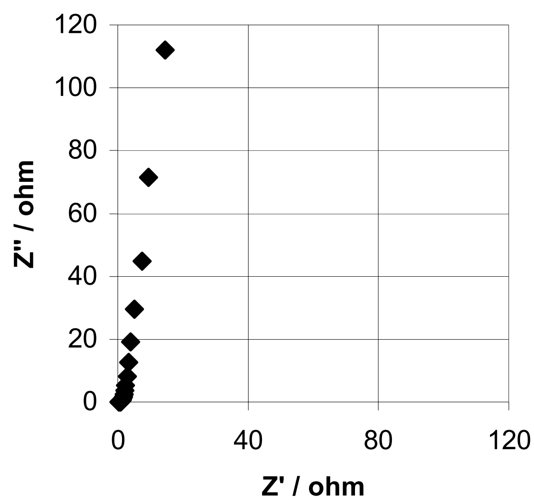

Figure 2. Impedance spectroscopy characteristic for the carbon sample A-PM. Mass of electrodes: 12.2/12.8 mg. C = 273 F g^{-1} (at 1mHz)

It is important to stress that the capacitive behaviour of the microporous carbons could be further improved by enhancing the mesopore volume. The presence of mesopores plays a crucial role for the ions transportation to the active surface. Hence, a development of mesopores and a strict control of the micropore-mesopore volume ratio is necessary.

For practical application cycleability of capacitor is an important characteristics. Figure 3 shows cyclic durability of capacitors. Capacity was measured during subsequent cycles at current load of 165 mA/g. Stable values were observed for the most of samples.

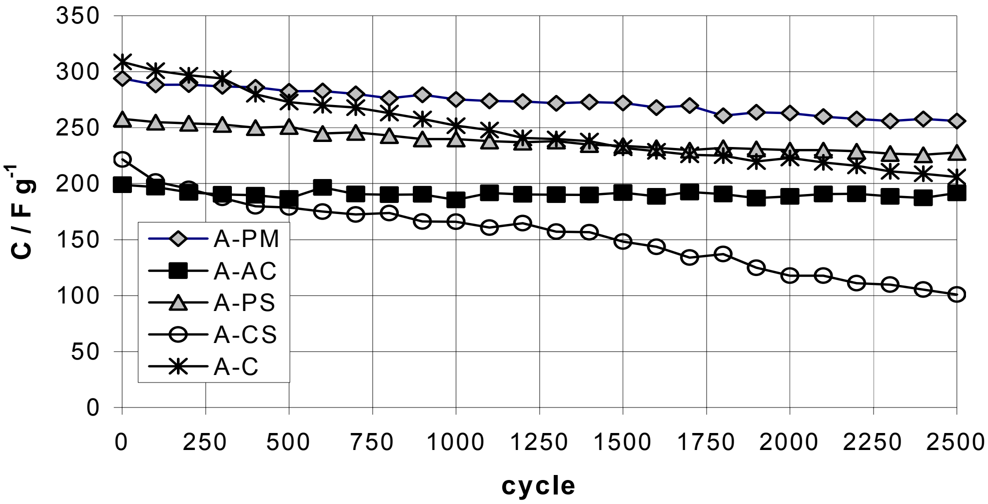

Figure 3. Cycleability of capacitors built from KOH activated carbons

Conclusions

The KOH activated carbons give excellent capacitance values reaching ca. 300 F g^{-1} despite a rather moderate specific capacitance per surface area, being in the range of 7-11 μF cm^{-2}. Apparently, this can be considered as due to a restricted accessibility to the micropores active surface. It seems that the carbon A-PM from mesophase pitch because of a good precursor organization gives pores of more adapted size as a consequence of intercalation phenomena during KOH activation. Hence, A-PM is a definitively better candidate for capacitor electrode than the other investigated carbons. A detailed analysis proved that wide micropores and narrow mesopores play a crucial role for ions transportation during charging of the electrical double layer using carbons with extremely developed surface area. Additionally, the low cost of the carbons based on natural precursors makes them extremely attractive for capacitor application. However, for a long-term capacitor performance, the carbons with a low leakage current and limited self-discharge should be selected to fulfil the practical demand.

References

[1] Conway BE. Electrochemical supercapacitors-scientific fundamentals and technological applications, New York: Kluwer Academic/Plenum, 1999.
[2] Frackowiak E, Beguin F. Carbon materials for the electrochemical storage of energy in capacitors. Carbon 2001;39:937-950.
[3] Qu D. Studies of the activated carbons used in double-layer supercapacitors. J. Power Sourc. 2002;109:403-411.
[4] Kierzek K, Frackowiak E, Lota G, Gryglewicz G, Machnikowski J. Electrochemical capacitors based on highly porous carbons prepared by KOH activation. Electrochim Acta 2004; 49:515-523.
[5] Lozano-Castello D, Lillo-Rodenas MA, Cazorla-Amoros D, Linares-Solano A. Preparation of activated carbons from Spanish anthracite. Carbon 2001;39:741-749.