Charcoals Used as Electrode Material in Supercapacitors

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***Abstract-* In this paper we have been described biomimetical structured charcoals based on acacia, sycamore, coconut and pine, in which capacitance arises in consequence of separation of charges in electrode/electrolyte interface (so-called electrical double layer), due to it's biomimetical structure, are proven to have high porosity and capacitance.**

Influence of biomimetical structure on supercapacitive behaviour has been tested by cyclic voltammetry, galvanostatic charge-discharge and self-discharge tests.

I. INTRODUCTION

During whole history of mankind people were trying to draw inspiration from the nature to make their lives better. In the middle of XX century this tendency lead to rise of a new interdisciplinary field of science – biomimetics. So far a large amount of new materials has been discovered e.g.: very light biomorphic cellular ceramics with high thermal and mechanical strength [1], artificial bones made from hydroxyapatite [2], SiOC cellular ceramics used in biomedicine and electronics [3], or lightweight, porous ceramics structures for catalytic use [4, 5].

In recent years investigations on a new type energy storage device, so-called supercapacitor, has been carried out intensively. In supercapacitor high surface area of porous carbon electrode and the phenomenon of electrical double layer at electrode interface is used to obtain high capacitance, power and energy density.

The natural structure of a living tree found to be very porous. This natural porosity is connected with existence of special tissues responsible for a transport of water and soluble mineral nutrients from the roots to the rest of the plant. This natural porosity can be used to obtain an interesting material for supercapacitor electrode.

In this paper different types of pyrolyzed and activated woods was tested as an electrode in supercapacitor.

II. EXPERIMENTAL

A. Preparation of pyrolyzed and activated charcoals

Previously cutted out and prepared raw samples of four types of trees: acacia, sycamore, coconut and pine were carbonized in tubular furnace in controlled atmosphere of Ar gas for 2 hours at 1100 ºC. Then samples were activated by treating solid KOH at 700 ºC for 90 min. The initial amount of substrates in weight relation was 1.0 KOH / 0.25 wooden substrate. Charcoals produced that way was then formed in defined shapes and weighted.

B. Electrochemical tests

Previously cutted out and prepared, raw samples of charcoal was tested as supercapacitor electrodes; 1M solution of H_2SO_4, and 6M KOH were used as an electrolyte. All measurements were made in five electrodes system using a device ATLAS 0531 Electrochemical Unit & Impedance Analiser. The reference electrode was saturated calomel electrode.

The range of taken tests:

- Cyclic voltammetry
- Galvanostatic charging and discharging
- Self-discharge tests

III. RESULTS AND DISCUSSION

A. Cyclic voltammetry

Cyclic voltammetry measurements was carried out at a rate of potential increase 1 mV/s to the value of 1.1 V, back to the zero, and then for a negative potential equal -1.1 V and again back to zero.

Analysis of the shape of voltammetric curve (CV) gives an information about electrochemical phenomenon in system, especially about electrodes phenomenon, resistance of system and dynamics of electrical double layer charging and discharging. The width of hysteresis loop corresponds to the ability of electric charge accumulation and is a basis of supercapacitor capacitance calculation. Fig. 1a, 1b, 1c, 1d shows CV for different types of charcoal, before and after activation in 1M H_2SO_4 and 6M KOH.

Activated charcoals are seemed to have wider hysteresis loop, than charcoals before the activation, for both acidic and basic electrolyte. Also the current response are considerably higher than in charcoals before the activation.

B. Galvanostatic charging and discharging

Galvanostatic charging and discharging measurements are very helpful in calculation of supercapacitor capacitance. To charge and discharge the supercapacitor forced, constant

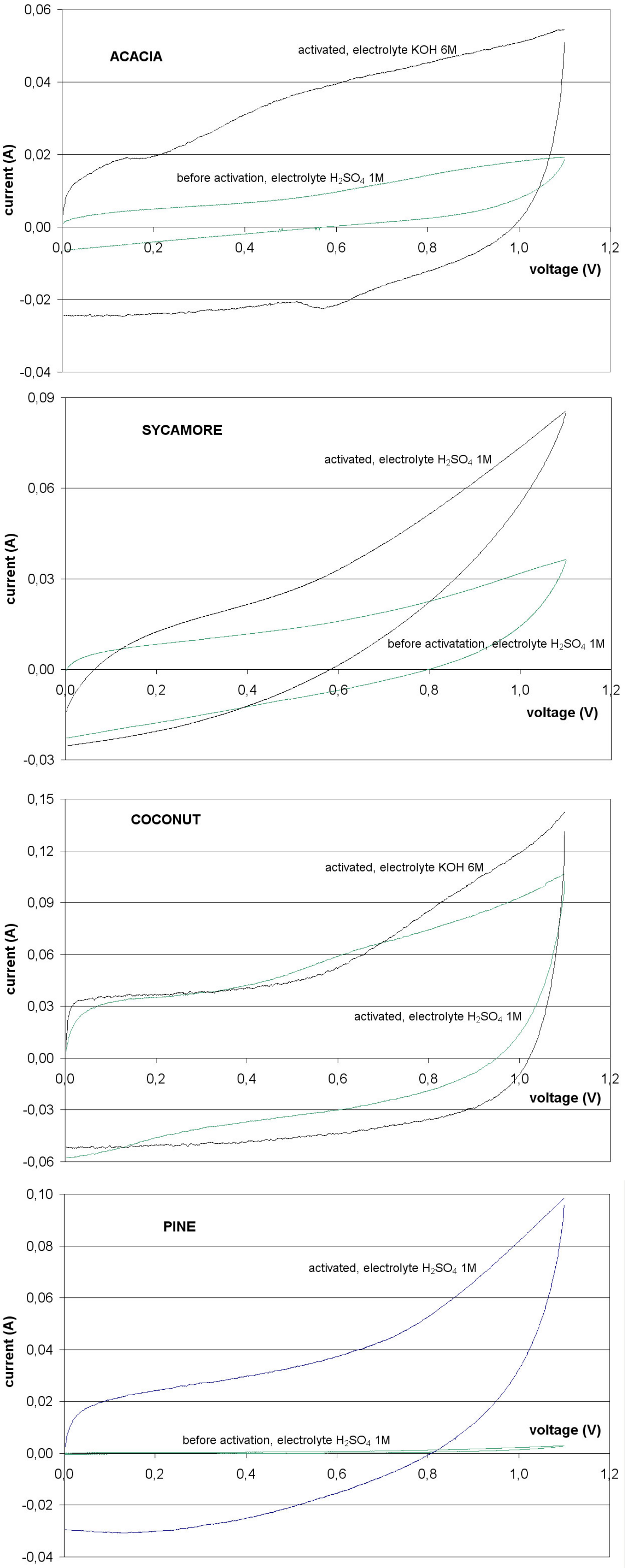

Figure 1. Diagram of cyclic voltammetry for (a) acacia , (b) sycamore, (c) coconut, (d) pine; scan rate 1 mV/s.

current was held and the time when potential between cell electrodes reach previously fixed value was the variable. In this case the current value was set as 1/5 of absolute value of potential, e.g. if potential was set as 600 mV, current was 120 mA. The supercapacitor was charged and then discharged for the following values of cell potential: 100, 200, 300, 400, 500 and 600 mV.

Results of galvanostatic charging and discharging measurements was gathered in Table I. The capacitance of supercapacitor was recalculated with respect to the mass of electrode.

Activation of charcoals are supposed to have a great influence on their capacitive bahaviour. In all cases the capacitance is much higher than before the activation, e.g. pine (Fig.1d), where the capacitance is more than hundred times higher. Also it is worth to be noticed that in 6M KOH electrolyte the capacitance is considerably higher than in acidic one (with the exception of activated sycamore).

C. Self-discharge tests

There are many factors that have influence on the behaviour of supercapacitor self-discharge, e.g. ionic mobility, sort and strength of electrolyte, temperature, degree of solvation, factors responsible for matching electrolyte and electrode: wettability, size of electrode pores, and ions of electrolyte.

In measurements supercapacitor was charged to the potential 0,6 V at a rate of potential increase 10 mV/s. This potential was forced for 10 minutes using external power source and then was controlled for the next 11 hours.

The results of measurements was presented in Table II and in Fig. 2.

Leakage current is very important parameter in self-discharge analysis, it determines the amount of energy needed to sustain the electrical double layer. Low leakage current connected with high capacitance, as in activated acacia,

TABLE I

Galvanostatic Measurements - Capacitance Of Charcoals In Acidic And Basic Electrolyte

Sample		Capacitance [F/g]	
		1M H_2SO_4	6M KOH
1	Acacia	27,9	
2	Acacia - *activated*	79,9	170,6
3	Sycamore	58,8	-
4	Sycamore - *activated*	141,6	82,6
5	Coconut - *activated*	220,8	281,5
6	Pine	3,9	-
7	Pine - *activated*	475,8	-

TABLE II
SELF-DISCHARGE BEHAVIOUR FOR DIFFERENT KINDS OF CHARCOALS, IN ACIDIC AND BASIC ELECTROLYTE

Sample		self-discharge after charging to 600 mV	
		leakage current [mA]	potential after 1 hour [mV]
1	Acacia, H_2SO_4	4,1	155
2	Acacia – *activated,* H_2SO_4	5,0	135
3	Acacia – *activated, KOH*	1,6	379
4	Sycamore, H_2SO_4	4,0	437
5	Sycamore – *activated,* H_2SO_4	9,3	246
6	Sycamore – *activated, KOH*	3,0	422
7	Coconut – *activated,* H_2SO_4	10,8	286
8	Coconut – *activated, KOH*	3,1	529
9	Pine, H_2SO_4	0,2	104
10	Pine – *activated,* H_2SO_4	10,1	360

sycamore and coconut, is very desirable factor for supercapacitors. It is worth to be noticed that in acidic electrolytes leakage current is over three times larger than in basic ones.

IV. CONCLUSIONS

On the basis of the electrochemical measurements it was concluded that the activation of charcoals is crucial for their capacitance, charge, discharge and self-discharge behaviour.

For all samples supercapacitive properties are seemed to be considerably greater than before the activation. The charcoals obtained in this way appeared to have hydrophilic (activated coconut and sycamore) or hydrophobic properties (pine and sycamore before the activation).

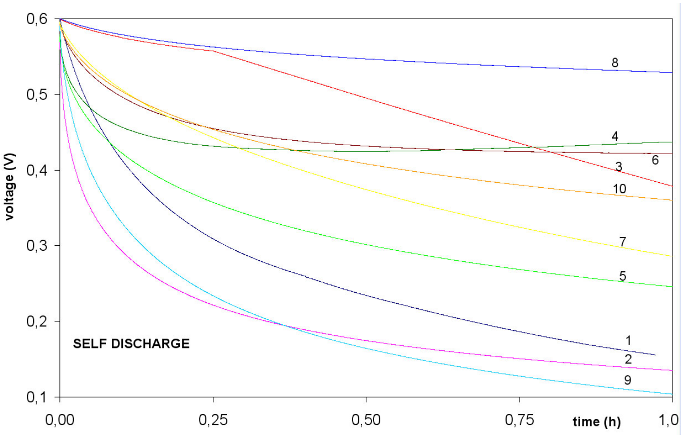

Figure 2. Diagram of self-discharge of supercapacitor after charging to 600 mV (1) acacia, H_2SO_4, (2) acacia – *activated,* H_2SO_4, (3) acacia – *activated, KOH,* (4) sycamore, H_2SO_4, (5) sycamore – *activated,* H_2SO_4, (6) sycamore – *activated, KOH,* (7) coconut – *activated,* H_2SO_4, (8) coconut – *activated, KOH,* (9) pine, H_2SO_4, (10) pine – *activated,* H_2SO_4.

As a result of voltammetric measurements charcoals in which in range of charging potentials unfavourable electrochemical processes(decomposition of water) does not exist was selected: coconut and pine.

REFERENCES

[1] H. Sieber, Ch. Hoffmann, A. Kaindl, P. Greil, *Biomorphic Cellular Ceramics*, Advanced Engineering Materials (2000), 2. No. 3, pp. 105 – 109.

[2] K. Hata, T. Kokubo, *Growth of a Bonelike Apatite Layer on a Substrate by a Biomimetic Process,* J. Am. Ceram. Soc.(1995), 78, 4, pp. 1049-1053.

[3] P. Colombo, *Novel Processing of Silicon Oxycarbide Ceramic Foams,* Advanced Engineering Materials, (1999) 1, No.3-4, pp. 203-205.

[4] T. Ota, M. Imaeda, H. Takase, M. Kobayashi, N. Konoshita, T. Hirashita, H. Miyazaki, Y. Hikichi, *Porous Titnia Ceramic Prepared by Mimicking Silicified Wood*, J.Am. Cer. Soc. (2000) 83, 6, pp. 1521-1523.

[5] T. Ota, Y. Hikichi, H. Unuma, M. Takahashi, H. Suzuki, H. Akahane, *Production of Ceramic Woods by Mimicking Fossil Woods,* 9-th Cimtec-World Ceramic Congress, Ceramic Getting ito the 2000`s – Part C (1999), pp. 531-538.

[6] B.E. Conway, *Electrochemical Capacitors: ScientiJic Fundamentals and Technological Applications,* Kluwer AcademicPlenum, 1999.