CHARACTERIZATION OF POROUS STRUCTURE AND ELECTROCHEMICAL PROPERTIES OF SYNTHETIC ACTIVE CARBONS FOR ELECTRIC DOUBLE LAYER CAPACITORS

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INTRODUCTION

Electric double layer capacitors (EDLC) with carbon materials and electrolytes have been widely used in different energy storage technologies [1]. Electric double layer capacitors consist of a pair of polarizable carbon electrodes, current collectors, a separator, and an electrolyte. Electric charge is stored in the electric double layer at the interface between carbon materials and electrolyte when voltage is applied. The double layer is discharged during operation.

The different carbon materials: activated carbon fibers [1,2,4] and cloths [4]; carbon microbeads [2] and powders [1,2]; carbon blacks [1,3]; carbon nanotubes [3] and others are used as the active materials for the production of electrodes for EDLC. The more suitable material for supercapacitor electrode must have the high surface area with significant value of specific double layer capacitance, high electrical conductivity, electrochemical stable surface in acid and alkaline media.

Synthetic active carbons (AC's) prepared from polymers and resins are used as effective sorbents, carriers for catalysts and electrode materials. These carbons are characterized by the well-developed micro- and mesoporosity, high surface area, low ash content and unique physical and electrochemical properties [5].

In the present paper the data on influence of porous structure, surface chemistry and some electrochemical properties of synthetic AC's on the capacitance and operating characteristics of EDLC are analyzed.

EXPERIMENTAL

Synthetic AC's were prepared by carbonization and followed steam activation of some types of porous styrene and vinylpyridine copolymers [5,6]: carbons series ST and VP correspondingly. By varying initial copolymer, conditions of carbonization and activation, AC's with different micro- and mesoporous structure were obtained.

The characterizations of carbons' structure were carried out by means of physical adsorption of nitrogen at 77 K and by mercury porosimetry method. The parameters of microporous structure (volume (V), average size (L_{mi}) and surface area (S_{mi}) of micropores) were determined from isotherm of nitrogen adsorption using Dubinin-Radushkevich equation by means described elsewhere [7]. The pore size distribution of micropores in AC's was evaluated according to Dubinin-Stoeckli equation [7]. The volume, surface area (S_{me}), average radius (R_{me}) and PSD of mesopores were calculated by using mercury porosimetry data by means of special developed computer software "RTUT".

Experimental supercapacitors of coin type (23 mm diameter and 2,5 mm thickness) were fabricated from powdered synthetic AC, graphite powder and water-Teflon emulsion as a binder. Three types of electrolytes are used: 28% weight KOH aqueous solution, 1M $LiClO_4$ solution in propylene carbonate and 0.7 M $(Et)_4NBF_4$ solution in acetonitrile. The parameters of capacitance and store energy were measured in galvanostatic regime under currents 0.05-0.5 A by using a special monitoring system "MACCOR". The capacitance was calculated by multiplying the current by inverse slope of the voltage discharge curves. The internal electrical resistance of EDLC was determined by means of impedance spectrometer "Shlumberger" at the frequency of 1 kHz. Table 1 shows the operating performance of the experimental supercapacitors using ST carbon.

Table 1. Performance summary for EDLC using synthetic active carbon ST

Type	Electro-lyte	Capacitance F	Voltage V	Store energy J/g(cell)	Resistance mOhm
SCA	aqueous	8.3	1.2	22.8	48
SCO	organic	5.2	3.0	32.4	313

RESULTS AND DISCUSSION

The data on capacitance of electric double layer (EDL) for KOH electrolyte, calculated per weight of active mass and parameters of porous structure of synthetic AC's are presented in Table 2. The micropore size distribution for two samples of carbons are shown in Fig.1. The synthetic AC's have bimodal pore structure with well developed systems of micro- and mesopores. The existence of biporous structure of AC's is extremely important for capacitor electrodes, because of the combination of micro- and mesoporosity not only gives the high specific capacitance, but provides a high micropore accessibility.

Table 2. The parameters of specific capacitance and pore structure of synthetic active carbons

Carbon	C, F/g	S_{mi}, m^2/g	L_{mi}, nm	S_{me}, m^2/g	R_{me}, nm
ST	160	790	0.74	120	12
STO	190	737	0.76	132	12
VP	136	1165	1.09	67	35

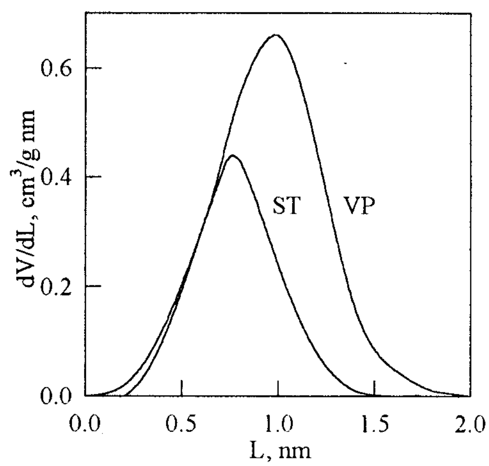

Fig.1. Pore size distribution for synthetic active carbons ST and VP types.

It was found that specific capacitance (C) of synthetic AC's depends on both of micro- and mesopores. The analysis of the data according to equation:

$$C = C_{mi} S_{mi} + C_{me} S_{me} ,$$

proposed by H. Shi [1] gives the values for capacitance of EDL in micropores C_{mi} =0.078 F/m^2 and C_{me} = 0.70 F/m^2 in mesopores, which are in a good agreement with data reported in [1,8]. The increasing of micropores surface by means of preparation of AC's with smaller micropore size leads to nonstable EDL for organic electrolytes.

The higher capacitance of mesopores may be connected with the supposition that the surface of mesopores of AC's is formed by edge planes of carbon microcrystallites, which have EDL capacitance in the range 0.50-0.70 F/m^2 [8]. The high capacitance for edge plan is attributed to the high surface roughness and the capacitive contribution of the surface groups.

The effect of oxygen containing groups is demonstrated in Table 2 for samples ST and STO. These carbons have approximately the same porous structure, but the sample STO, which was oxidized and initially contained 1.9 mmol/g of acid groups, shows the higher capacitance. Hence the introducing of surface oxide groups leads to increasing of EDL capacitance without visible decreasing of electric conductivity of carbons.

The thermal treatment of AC's in inert atmosphere has a double effect. On the one side the increasing of the temperature results in increasing of the carbon matrix conductivity, but on second one leads to decreasing of the EDL capacitance. Hence the selection of the maximum temperature of the heat treatment must be the reasonable compromise between these two effects.

The potential of zero charge (PZC) of carbon surface is also an important electrochemical characteristic of carbon materials for EDLC. The PZC of synthetic AC's is located in the range from -0.1 to +0.05 V, therefore these materials are demonstrated the minimum disbalance between cathodic and anodic capacitance, and have practically symmetrical curves for cyclic voltammograms.

Therefore the using of synthetic AC's as active material for electrodes was resulted to the creation of coin type EDLC with improved operating performance and long cycle life.

REFERENCES

1. The 4th Intern. Seminar on Double Layer Capacitors and Similar Energy Storage Devices. Deerfield Beach, USA, 1994.
2. Hang Shi, in Carbon'95 (Ext. Abstr. 22nd Biennial Conf. Carbon) San Diego, CA, 1995, pp.826-827.
3. K.Lafdi, J.Clay, ibid., pp.824-825.
4. I.Tanahashi, A.Yoshida, A.Nishino, Carbon, 1990, **28**, 477; Carbon, 1991, **29**,1033.
5. V.Strelko, in Carbon'90 (Ext. Abstr. European Carbon Conf.), Paris, France, 1990, pp.16-17.
6. A.Bagreev, V.Strelko, J.Lahaye in Carbon'96 (Ext. Abstr. European Carbon Conf.), Newcastle Upon Tyne, UK, 1996, pp.527-528.
7. M.Dubinin, Carbon, 1987, **25**, 593.
8. K.Kinoshita, Carbon: Electrochemical and Physico-Chemical Properties. Wiley-Interscience, 1988.