Effect of aqueous electrolytes on electrochemical capacitor capacitance

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Introduction

Electrochemical capacitors, also called supercapacitors or ultracapacitors [1÷3], are attractive power sources because of their high power density, good durability and moderate energy compared to conventional dielectric capacitors and batteries. Electrochemical capacitors are used in systems that require short currents supply with high power densities, such as electric vehicles during their start-up, in the elements cooperating with solar cells to increase their power or in power backup systems (UPS) [4]. Energy storage in supercapacitors combines pure electrostatic interaction between the charged capacitor plates and the ions from the electrolyte solution and the processes associated with the redox reactions of electrode material. Usually, the electrical double layer capacitors use as electrode materials activated carbons with high specific surface area, metal oxides or conductive polymers, exploiting additional, faradaic type of interaction called pseudocapacitance. The application of materials with a high effective surface area and a pore structure which enhances the efficient exploitation of electrode surface, allows to obtain a very large capacitance values. The factors which influence capacitance values are as follows: the high surface area, the geometry and size of the pores. In case of electrode material pores the average size, good wettability and the presence of electroactive molecules are also of great importance [5]. There are intensive research to obtain new materials for electrodes and suitable electrolytes to capacitor application, which should be characterized by a large capacitance, cyclic stability and low cost. Capacitance is calculated on one electrode and it is proportional to the electrode/electrolyte surface (S), according to the equation:

$$C = \frac{\varepsilon S}{d} \quad (1)$$

where ε is the dielectric constant and d is the thickness of the electrical double layer. The thickness of the double layer depends on the concentration and ion size of the electrolyte. It is usually a size 2–10 Å for concentrated electrolytes.

The capacitance of the capacitor consists of two capacitor capacitances connected in series, according to the equation:

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

Specific capacitance can be related to the mass of the electrode (F/g), to the volume of the electrode (F/cm^3), or to the surface (F/cm^2) [6].

According to formula (1), increasing surface area of the electrode influences obtaining a higher capacitances. Due to the fact that a part of the pores is not available for the electrolyte and they do not take place in the formation of electric double layer, the obtained capacitance is not so high. It is assumed, that the pores which have size larger than the ions with the solvation shell are advantageous in order to reduce the relaxation constant (which describes the minimum time required to obtain all the energy stored in the capacitor with a efficiency greater than 50%) and increase the value of capacitance. Using porous electrode materials, with suitable structure matching the size of the electrolyte ions can improve the electrochemical characteristics of the capacitor. Suitable pore size distribution has greater influence on the capacitance than the effective surface area [7]. A significant increase in capacitance was observed for carbons with pores < 1 nm, where the pore size is close to the size of the ions. In addition, the limitation of the capacity related with the adsorption of the cations and anions with large size can be minimized by the addition of ions with smaller sizes [8]. The pores of the carbon material are available when their size matches the real size of the electrolyte ions.

In conclusion, it should be noted that the capacitance of the capacitor depends mostly on the capacity of electrode material expressed in F/g, while the voltage and the resistance of a such device depends mainly on the electrolyte. Carbon materials are used as the electrode materials but also as the composite components in symmetric devices. Due to the fact, that intensive research on electrode materials consisting of composite MnO_2 /carbon for electrochemical capacitors, are still in progress, the paper attempts to find the inert electrolyte, such as Na_2SO_4, Na_2SO_3, K_2SO_4, Li_2SO_4, (as well as for comparison 1 M H_2SO_4 and 6 M KOH) and estimate their effect on the capacitance of electrode materials (two activated carbons and carbon nanotubes) to the electrochemical capacitor.

Experimental

Physicochemical characterization of electrode materials

As the electrode materials were used: commercial activated carbon NORIT GSX (Alfa Aesar) and multi-walled carbon nanotubes NTs 7–15 (OD 7–15 nm, ID 3–6 nm, length 0.5–200 microns, > 95% (Aldrich)). Activated carbon, labeled CA was prepared by carbonization of commercial lignine (Aldrich) and then activated in KOH with a C:KOH ratio of 1:4. The prepared carbon was cleaned with HCl and HF. Carbon materials were characterized by scanning electron microscopy – SEM EVO® 40 ZEISS. Microporosity and surface area were determined by the BET method. To study the adsorption of nitrogen at 77 K, the analyzer from Micromeritics ASAP 2010 was used. Elemental analysis was performed using the analyzer Vario MICRO CUBE Elementar Analysen Systeme GmbH.

Conductivity of electrolytes

Electrolytes as follows: 1 M Na_2SO_4, 1 M Na_2SO_3, saturated K_2SO_4, 1 M $MgSO_4$ and for comparison 1M H_2SO_4 and 6M KOH were prepared. All reagents were for analysis grade from POCH and CHEMPUR. Electrolyte conductivities were estimated using the electrochemical impedance spectroscopy and conductometer CPC-505 (Elmetron). The electrochemical impedance spectroscopy is an indirect method of estimating conductivity and it is based on fitting the equivalent circuit to the results of measurements.

Electrochemical measurements

The electrochemical performance of carbon materials in symmetric capacitors were studied in two and three electrode Swagelok® systems using aqueous solutions of different salts as electrolytes. The specific capacitance of electrode materials was investigated by three electrochemical techniques: cyclic voltammetry (1–100 mV/s), galvanostatic charging/discharging (100 mA/g – 10 A/g) and electrochemical impedance spectroscopy (100 kHz-1mHz) using potentiostat – galvanostat VMP3/Z (Biologic, France). The capacitance values were expressed per active mass of one electrode. The materials with the highest capacitances have been subjected upon cycle stability (5000 cycles) with current regime 2 A/g.

Results and Discussion

Surface morphology

Surface morphology of the carbon materials were characterized by scanning electron microscopy. SEM images of carbon materials are showed in Figures 1–3. The activated carbons prepared by carbonization of commercial lignine demonstrated the ball-shaped morphology with visible pores, while in Norit GSX image some traces of precursor are well visible. Multiwall carbon nanotubes (Fig. 3) form a cluster of irregularly shaped, which looks like natural sea sponges.

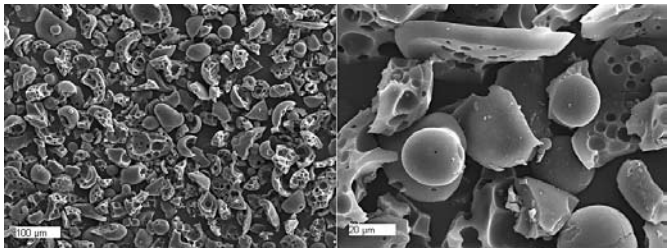

Fig.1. SEM images of CA activated carbon (obtained by carbonization and activation of the lignin)

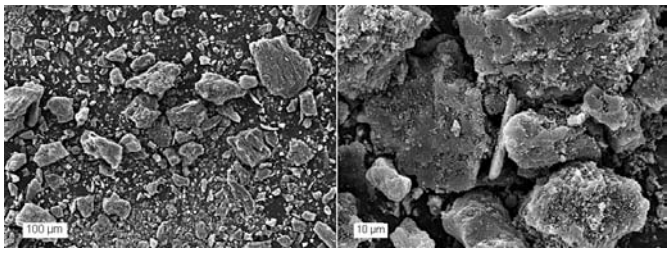

Fig. 2. SEM images of activated carbon NORIT® GSX (Alfa Aesar)

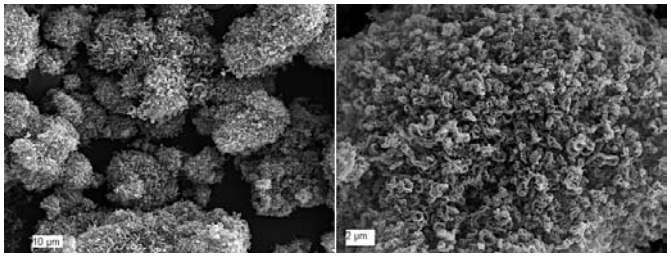

Fig. 3. SEM images of multiwalled carbon nanotubes NTs 7–15 (Aldrich)

The specific surface area and porosity

The adsorption model of Brunauer-Emmett-Teller (BET) was used to calculate the specific surface area. Figure 4 presents the nitrogen adsorption-desorption isotherms of two activated carbons and commercial carbon nanotubes.

The main nanotextural parameters of carbons are given in Table 1. The pore size distribution of carbon materials was evaluated according to the non-local density functional theory (DFT) approach and it is shown in Figure 5. Carbon materials with significantly different pore structure and specific surface area were selected to determine relationship between pore size and capacitances obtained in different electrolytes. Activated carbon (CA) has a large number of micropores which have influence on significant specific surface area, above 2300 m^2/g. The activated carbons (CA and Norit (946 m^2/g)) exhibited a similar I type isotherm (so-called Langmuir isotherm) according to the IUPAC with the H4 type of hysteresis loop, which is typical for microporous material. The pores have a shape of narrow gaps formed between the two planes. Adsorption isotherm of NTs 7–15 is examples of II type adsorption isotherms according to the IUPAC with H3 type of hysteresis loop, which is characteristic for mesoporous materials [9÷10].

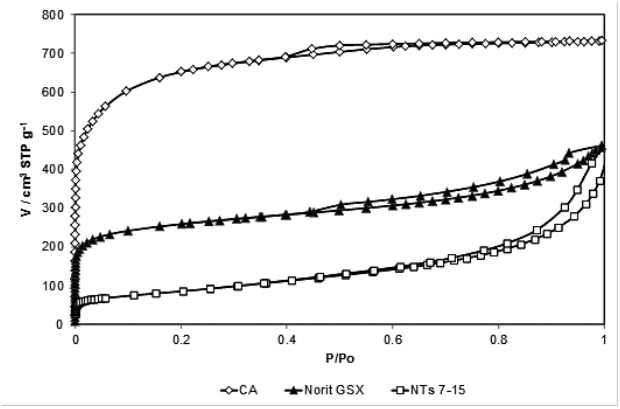

Fig. 4. Nitrogen adsorption isotherms (77 K) of carbon electrode materials

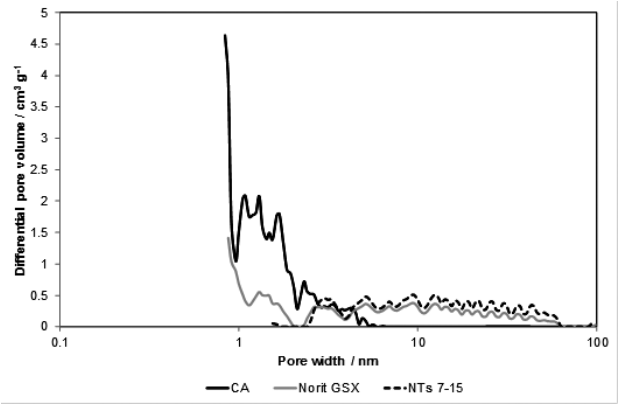

Fig. 5. The pore size distribution of carbon materials

Table 1

Surface area and pore size distribution

Electrode material	CA	NTs 7 15	Norit GSX
Specific Surface Area (BET), $m^2 g^{-1}$	2339	297	946
Micropore vol., $cm^3 g^{-1}$	0.882	0.062	0.323
Mesopore vol., $cm^3 g^{-1}$	0.147	0.453	0.321
Total pore vol., $cm^3 g^{-1}$	1.030	0.544	0.654

Elemental Analysis

The carbon content in the samples is given in Table 2. Due to the fact, that activated carbons contain heteroatoms and functional groups, the percentage of carbon is less than in case of the carbon nanotubes.

Table 2

Carbon content in electrode materials

	C , %	H , %	N , %	S , %
CA	87.55	0.399	0.0	0.200
NORIT GSX	85.040	0.415	0.02	0.248
NTs 7–15	97.78	0.264	0.01	0.146

Electrolyte conductivity tests

The conductivities of electrolytes were tested using electrochemical impedance spectroscopy method and conductometr CPC-505. Comparison of the obtained electrolyte conductivities is given in Table 3. The sulfuric acid and potassium hydroxide have the highest values of conductivity, more than four times higher comparing to other electrolytes.

Table 3

Comparison of the electrolyte conductivities

	Electrolyte	Conductivity σ, mScm^{-1}	
		from EIS method	from conductometr
1	1M H_2SO_4	409	372
2	6M KOH	508	565
3	saturated K_2SO_4	104	99
4	1M Na_2SO_3	99	84
5	1M Na_2SO_4	91	92
6	1M $MgSO_4$	56	49

Electrochemical characterization of electrode materials

Capacitance properties (F/g) were examined using the methods: cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy [7, 11, 12]. Examples of obtained electrochemical characteristics using various different electrode materials and the electrolytes are shown in the Figures 6÷8. During CV measurements, the highest values of capacitance for CA were obtained in 1 M Na_2SO_3, using slow scan rate. If the scan rate values rise, there are not so good charge propagation and the highest value of capacitance is achieved in 1 M H_2SO_4.

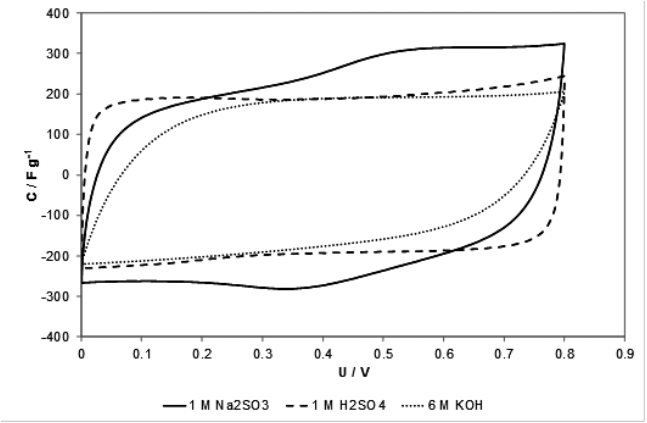

Fig. 6. Voltammetry characteristics of CA, two-electrode system (10 mV/s)

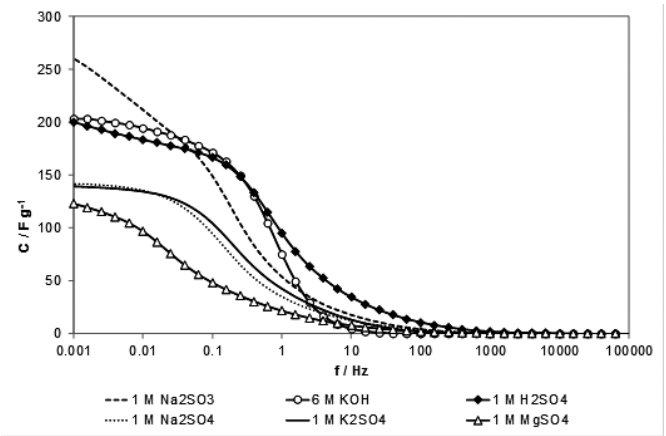

Fig. 7. Capacitance versus frequency dependence of CA in different electrolytes

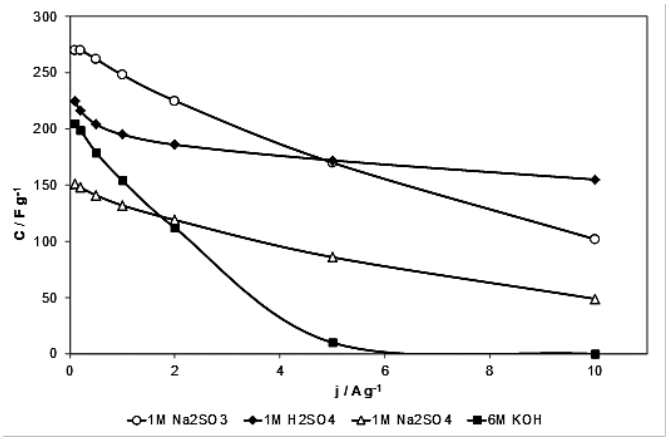

Fig. 8. Capacitance values versus current load for CA in different electrolytes

Capacitance versus frequency dependence of CA measured by the electrochemical impedance spectroscopy (EIS) is given in Figure 7. The highest capacitance in Na_2SO_3 is obtained at the low frequencies, whereas higher capacitances in sulfuric acid and potassium hydroxide are obtained at higher frequencies. Similar correlations were obtained from galvanostatic method, using a different current load. Capacitance values versus current load for CA in different electrolytes are shown in Figure 8. At low load currents maximum capacity is obtained in 1 M Na_2SO_3, but when the current density of 5 A/g is applied, the capacitance of CA fades drastically, especially in 6 M KOH and 1 M Na_2SO_3. The most stable capacitance values of CA are obtained in 1 M H_2SO_4. These results are also confirmed by the study of cyclic charge/discharge with current density of 2 A/g. The capacitance fade of CA after 5000 cycles in 1 M H_2SO_4 is ca. 2%. The highest values of capacitance ca. 220 F/g was obtained for CA in Na_2SO_3, with a decrease of capacitance after 5000 cycles about 6%. A slight decrease of capacitance for both electrodes after cycling is well visible using the electrochemical impedance spectroscopy method.

The lower values of capacitance were obtained for activated carbon Norit GSX. For that carbon, the highest values of capacitance were measured in electrolytes with the highest conductivity, i.e. in 1 M H_2SO_4 and 6 M KOH. In electrolytes which are characterized by highest conductivities, good charge propagation is visible, despite of the increase of scan rate or the increase of current density. For activated carbon Norit GSX the effect of the highest values of capacitance in Na_2SO_3 is not observed, as it was in case of carbon CA. This fact might be related to different distribution of pore size in the both carbons.

As it was expected, the lowest values of capacitance (a few F/g), from all measured carbon electrode materials, were obtained for carbon nanotubes. The highest values of capacitance, as well as for active carbon Norit GSX, were obtained in electrolytes, which are characterized by highest conductivity.

Conclusions

Aqueous solutions of acids, alkaline, inorganic salts and solutions of organic salts are used as the electrolytes in electrochemical capacitors. In this study, we used aqueous electrolytes as follows: Na_2SO_4, Na_2SO_3, K_2SO_4, $MgSO_4$ and for comparison 1M H_2SO_4 and 6M KOH. As the electrode materials two activated carbons and commercial carbon nanotubes, which have different composition, morphology and surface area were used. The highest values of capacitance were obtained for activated carbon CA with surface area more than 2300 m^2/g, where mainly, charging process of the electrical double layer take place. The lowest capacitance was obtained for the commercial carbon nanotubes. The conductivity of electrolytes was also examined. The highest values of conductivity were obtained for

1 M H_2SO_4 and 6 M KOH, while $MgSO_4$ has the lowest conductivity from electrolytes which were selected. For carbon CA (obtained from carbonized and activated lignin) the highest capacitance values were obtained in 1 M Na_2SO_3 solution, although that electrolyte has more than four times lower conductivity compared to 1 M H_2SO_4 and 6 M KOH. This dependency was not observed for the commercial activated carbon and carbon nanotubes. It may be assumed, that the most suitable pore structure of carbon CA is to Na_2SO_3 electrolyte. The conductivity of the electrolyte solution is not the only factor, which determines the obtained capacitance. Very important factor is a suitable porosity, matching the real size of the electrolyte ions to the pores of the electrode material.

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Translation into English by the Author

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