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THE IMPACT OF THE SURFACE MORPHOLOGY ON ENERGY CHARACTERISTICS OF NANOPOROUS CARBON MATERIAL

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Abstract: The impact of nanoporous carbon material (PCM) morphology on its electrochemical behavior in aqueous electrolyte has been studied. The optimum concentration of aqueous lithium sulfate which provides the maximum specific energy characteristics of capacitor-type systems C/Li₂SO₄/C is determined. Capacitive parameters of electrochemical capacitors (EC) in aqueous solutions of lithium, sodium and potassium sulfate which have different molar ratio have been studied by comparative analysis. Cyclic voltammograms at different scan rates show that the PCM capacitive behavior in three electrolytes increases in the following order Li₂SO₄<Na₂SO₄<K₂SO₄. This improvement could be a result of increasing the movement speed of hydrated ions in the volume of electrolyte and in the internal pores of PCM in the order Li⁺<Na⁺<K⁺. The obtained results give valuable information for the study of new hybrid supercapacitors.

Keywords: activated carbon material, double electric layer, electrolyte, specific capacity, internal resistance, electrochemical capacitor.

1. INTRODUCTION

Electrochemical capacitors that employ charge/discharge of the electrical double layer (EDLC) occupy an intermediate position between electrochemical batteries and conventional capacitors. The first part of the devices has high energy density with relatively low power density, and the second one has a relatively large capacity at sufficiently low energy density [3]. The increase in operating voltage of EC based on aqueous electrolyte is possible in the so-called hybrid capacitors (HC). It is a hybrid of a supercapacitor and a lithium-ion battery. A hybrid capacitor (HC) differs from a supercapacitor in discharge time (up to 1 hour) and energy density, which is higher with less number of recharge cycles [13]. As it follows from the ref. [2], the electrochemical system is based on a lithium manganese spinel as a cathode, and nanoporous carbon as an anode in Li₂SO₄ aqueous solution, has specific energy density to 30 J·kg⁻¹. As electrolytes based on Na₂SO₄ and K₂SO₄ salts are more affordable than Li⁺-based electrolytes, it is interesting to compare the energy characteristics of PCM in salt solutions of varying molar ratio.

HC energy characteristics largely depend on the specific capacity of the anode, which is made of PCM. In theory, the greater the surface area of PCM is, the higher specific capacitance is expected. However, the practical situation is more complicated. Experimental capacity usually depends on the

ratio between pore size distribution in carbon material and the size of solvated ions in the electrolytes [7, 8, 14]. The main reason is that nanopores with a small diameter are not available for electrolytic solution. The fact is that ions with their solvating shell are too big to get into nanopores. Therefore, the surface area with this type of nanopores does not make any contribution to the overall capacity of EDLC electrode material. For example, the radius of solvated ions in organic electrolytes is mostly larger than in aqueous electrolytes. As a result, the carbon electrode with a greater number of macropores, is mainly used in/with organic electrolytes [11, 12, 15]. In order to improve the specific energy characteristics of the EC one should study the interrelation of carbon material structural characteristics (specific surface area, pore size distribution and pore volume) for a particular electrolyte.

In this paper we investigate the correlation between structural and energy parameters of PCM which is used to make SC electrodes and HC anodes in sulphate aqueous solutions of lithium, sodium and potassium of varying molar ratio.

2. MATERIALS AND METHODS

As the object of study we use PCM obtained from a raw material of plant origin by hydrothermal carbonization of feedstock.

The process passes under pressure of water vapor $(12 \div 15) \cdot 10^5$ Pa and further thermal activation at temperature of 673 ± 3 K [9].

Determination of structural and adsorption characteristics of the material was carried out use of nitrogen adsorption at temperature $T = 77$ K by surface area analyzer Quantachrome Autosorb (Nova 2200e). The samples were previously degassed in a stream of helium at 453 K during 20 h. The calculation of adsorption isotherms allowed to obtain pore size distribution, specific surface area and specific pore volume. Electrochemical studies were conducted in a two-electrode cell (type "2525") with the spectrometer Autolab PGSTAT/FRA-2. EC electrodes were made from the mixture:

$$\langle PCM \rangle : \langle CA \rangle : \langle BM \rangle = \langle 75 \rangle : \langle 20 \rangle : \langle 5 \rangle,$$

where *CA* is a conductive additive (acetylene carbon black, graphite KS-15 of «Lonza» company), *BM* is a binding material (F-42L) [4]. In order to study specific capacity that depends on the rate of the EDL charge/discharge process we used a volt-ampere method with scanning rates from 1 to 50 $\text{mV} \cdot \text{s}^{-1}$. The rate of voltage change on the EC:

$$s = \pm \frac{dU}{dt}$$

and the corresponding capacitor current is associated with capacity by the equation

$$I = C \frac{dU}{dt}$$

or

$$I = Cs$$

PCM specific capacity is calculated by the formula:

$$C_{sp} = \frac{2I}{sm}$$

where *I* is the current of anodic or cathodic branches of a current-voltage curve, *s* is a scanning rate, *m* is an active electrode mass. The specific capacity of carbon material depends on discharge current,

which varied with a range of 1 and 50 mA, and is calculated by a galvanostatic method. The specific capacity of PCM was calculated by using the formula:

$$C_{sp} = \frac{I \cdot t_p}{(U - \Delta U) \cdot m}$$

where I is a discharge current, t_p is discharge time, $U - \Delta U$ is the potential difference between the extreme points of the discharge curve, m is mass of PCM.

Internal resistance is determined by a potential jump after 10 cycles of charge/discharge.

$$\Delta U = 2IR$$

where ΔU is a potential jump at discharge.

3. RESULTS AND DISCUSSION

In carbon particles pores of different size, shape and volume formed depending on the time of thermal activation. For research we selected carbon material, which had the maximum specific surface area and micropore volume.

The specific surface area was calculated by the multipoint BET method with a linear dependence of $1/[W(P_0/P) - 1]$ on P/P_0 in the adsorption isotherm P/P_0 range from 0.05 to 0.35. The total volume of pores with a radius less than 152.43 nm was determined under pressure of saturation, $P/P_0 = 0.99$. The average pore diameter was calculated according to the method of Horvath-Kawazoe. Table 1 shows the structural and adsorption characteristics of PCM.

| Parameter | PCM |
|--|--------|
| Surface area Multipoint BET, $S_a(m^2 \cdot g^{-1})$ | 800±20 |
| Total pore volume, $V_{total}(cm^3 \cdot g^{-1})$ | 0.4179 |
| Volume of micropores, $V_m(cm^3 \cdot g^{-1})$ | 0.2962 |
| Surface area of micropores, $S_m(m^2 \cdot g^{-1})$ | 722.5 |
| Average pore diameter, $D_{HK}(\text{Å})$ | 7.224 |

Tab. 1. Structural and adsorption characteristics of PCM

The adsorption isotherm analysis (Fig. 1, a) of PCM made it possible to determine the specific surface area, total pore volume and distribution both in size and volume (Fig. 1).

Electrochemical studies of carbon materials were performed in 0.5M, 1M, 2M, 3M and saturated aqueous salt solution of Li_2SO_4 . Cycle volt-ampere curves of electrochemical capacitors with these electrolytes are shown in Fig. 2.

At low scanning rates the curves of all five electrolytes are close to symmetrical rectangular shape without any peaks which are responsible for the occurrence of redox processes in the system. This waveform is a typical capacitive behavior of EC. With increasing the scanning rate the deviations from the ideal rectangular shape occur due to the reduction of movement time of solvated ions along working pores.

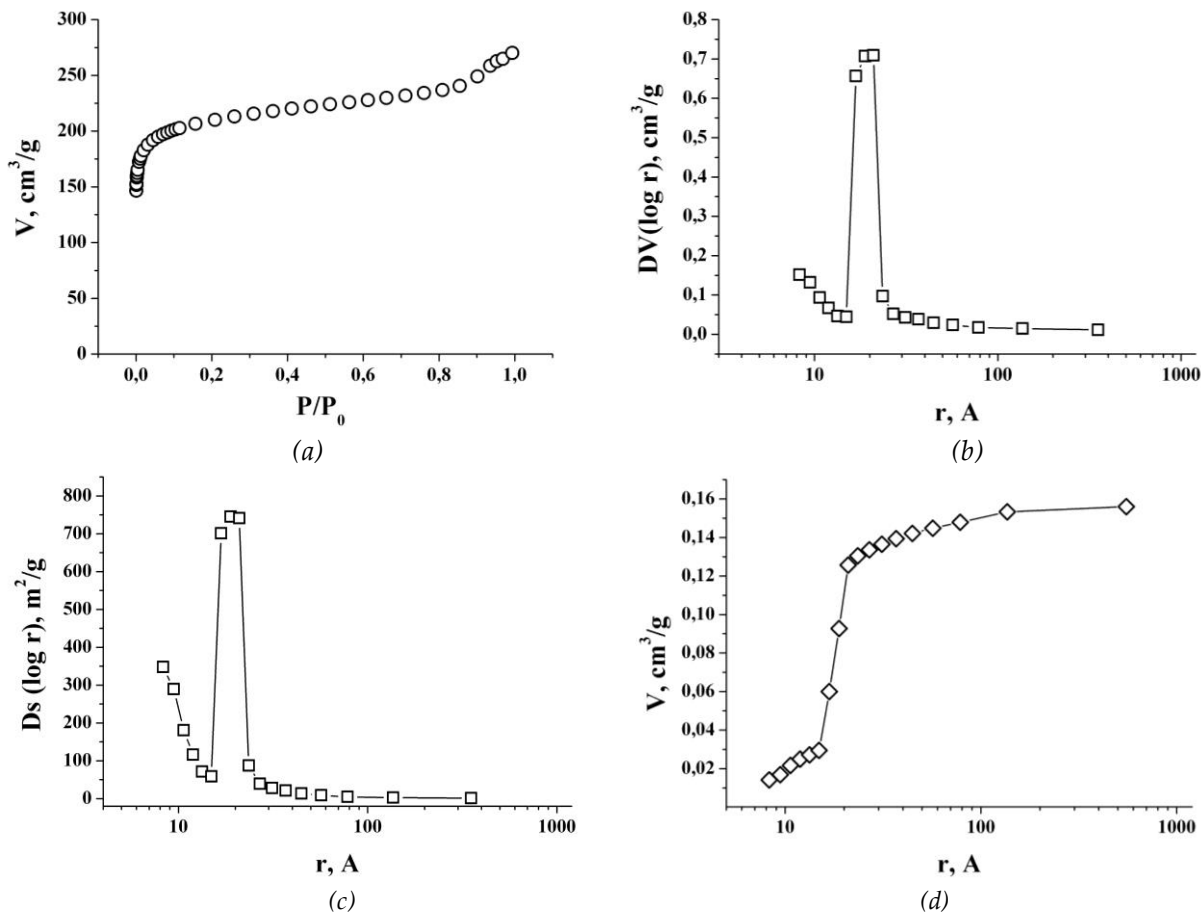


Fig. 1. Adsorption isotherm of nitrogen (a), pore size distribution (b), dependence of specific surface area on pore radius (c), dependence of pore volume on pore radius (d)

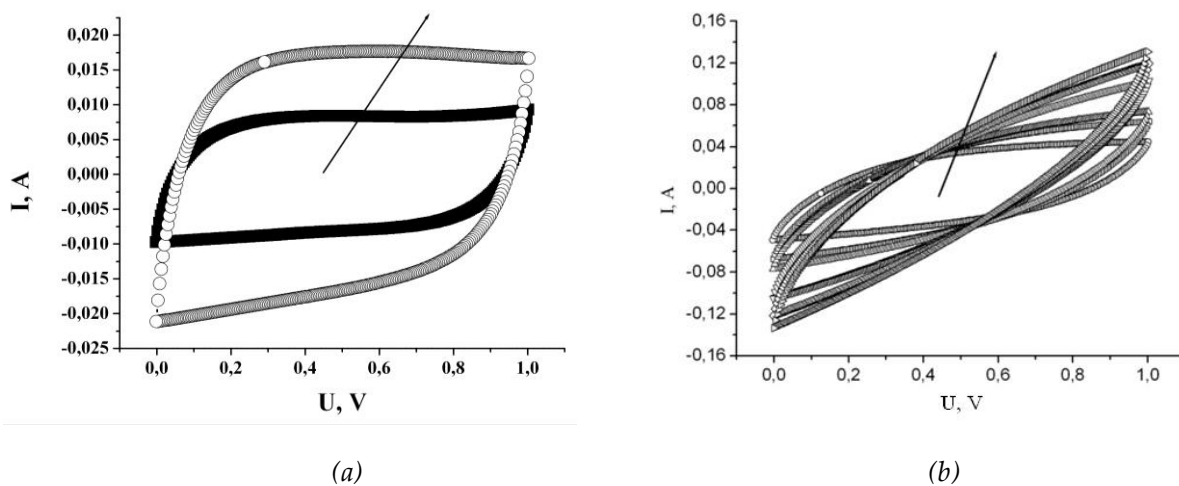


Fig. 2. Cycle volt-ampere characteristics of PCM in 2M aqueous solution of Li₂SO₄. Scanning rates: (a) 1, 2 mV·s⁻¹, (b) 5, 8, 10, 20, 30, 40 mV·s⁻¹ (arrow indicates the direction of the scanning rate increase s)

To study the capacitive behaviour of PCM in these electrolytes, the dependence of the specific capacity on the potential change rate of the cell was investigated.

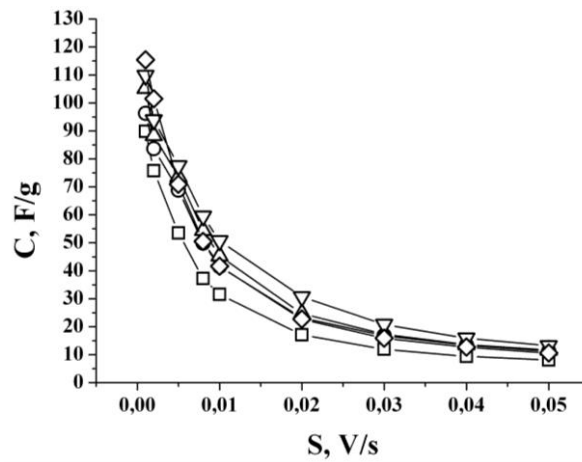


Fig. 3. Dependence of specific capacity of PCM in aqueous solution of Li_2SO_4 on scanning rate for electrolytes of various molar ratio: 0.5 M \square , 1 M \circ , 2 M Δ , 3 M ∇ , saturated \diamond

Figure 3 shows that at low scanning rate (up to $5 \text{ mV}\cdot\text{s}^{-1}$) carbon material in saturated aqueous salt solution of Li_2SO_4 has the highest specific capacity. It is associated with maximum concentration of electrolyte ions and low charge rate, providing sufficient time for EDL formation. With the increase of the scanning rate (5 to $30 \text{ mV}\cdot\text{s}^{-1}$) carbon material has a maximum capacity in 3M aqueous salt solution of Li_2SO_4 . In our view, it has an optimal ratio between the electrolyte ions concentration and their mobility, providing maximum capacity of EDL. For all samples with the increase of the scanning rate above $10 \text{ mV}\cdot\text{s}^{-1}$, there is a decrease of specific capacity, which can be explained by low mobility of ions within certain micropores. In the studied carbon materials there is an insufficient number of transport pores, which provide free access of electrolyte ions to the micropores, and the volume of micropores of radius $1.8 - 2.2 \text{ nm}$ amounts to 70% of the total pore volume. Therefore, a high scanning rate increases a number of micropores, in which the EDL is not formed completely and results in the reduction of specific capacity of PCM at high charge/discharge rates.

A sharp voltage drop at constant discharge current reveals the presence of ohmic resistance of the supercapacitor. According to ref. [5], the voltage drop $\Delta U_R = IR$ is defined as an intersection point between the voltage curve, which is linearly extrapolated and the axis of time immediately after the discharge circuit is closed. If a voltage drop exceeds 20% of the maximum, discharge current should be reduced twofold, fivefold or tenfold times. Fig. 4 shows the dependence of PCM capacity and voltage drop on the applied discharge current.

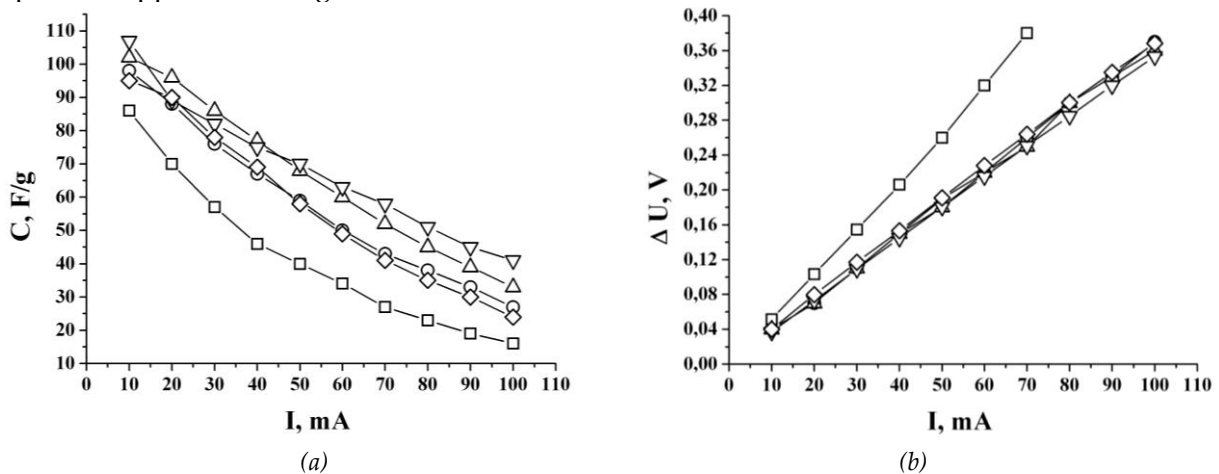


Fig. 4. Dependence of specific capacity of PCM (a) and voltage drop (b) on discharge current in aqueous solution of Li_2SO_4 for electrolytes of various molar ratio: 0.5 M \square , 1 M \circ , 2 M Δ , 3 M ∇ , saturated \diamond

For all samples the specific capacity decreases with the increase of discharge current (Fig. 4, a), and the maximum operating discharge current is up to 50 mA. With further increase in current the voltage drop exceeds 20% of the maximum voltage during the discharge.

To determine the occurrence of possible chemical reactions for PCM in 0.5 M aqueous salt solution of Li_2SO_4 , Na_2SO_4 and K_2SO_4 the electrochemical research into potential $0 \div 1$ V was performed. Fig. 5 shows cyclic volt-ampere characteristics with the scanning rate of 1 and 20 $\text{mV}\cdot\text{s}^{-1}$, respectively.

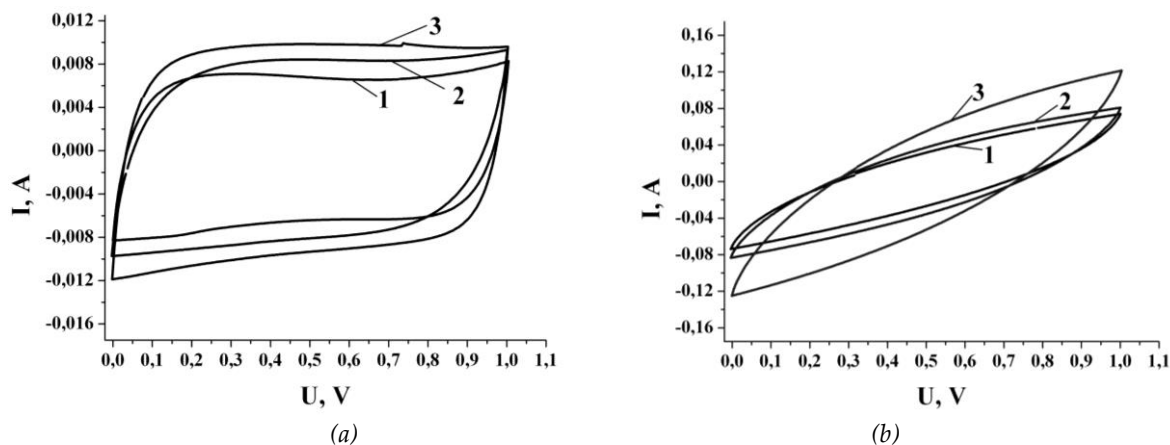


Fig. 5. Potentiodynamic curves for PCM in 0.5M aqueous solution of 1 – Li_2SO_4 , 2 – Na_2SO_4 i 3 – K_2SO_4 at scanning rate 1 mV/s (a), 20 mV/s (b)

When scanning rate numbers 1 $\text{mV}\cdot\text{s}^{-1}$ VA-curves of all the three electrolytes show a symmetrical shape close to rectangular without any noticeable redox peaks that are characteristic of capacitive behavior. The values of specific capacity of PCM in three electrolytes obtained at low scanning rates also do not show any significant differences, either. As a result of the relaxation time for movement of solvated ions at high scanning rate, all the curves deviate from the ideal rectangular shape and the capacity value in aqueous electrolytes increases in the order $\text{Li}_2\text{SO}_4 < \text{Na}_2\text{SO}_4 < \text{K}_2\text{SO}_4$.

Whereas there are no visible peaks on the volt-ampere characteristics obtained, as is the case of galvanic cells (batteries supply), it can be argued that the electrolyte has a chemical and electrochemical stability in the attached potential field [1].

Getting cyclic volt-ampere curves made it possible to calculate the specific capacity C_n of the investigated PCM. Dependence of the material specific capacity on the scanning rate is shown in Fig. 6.

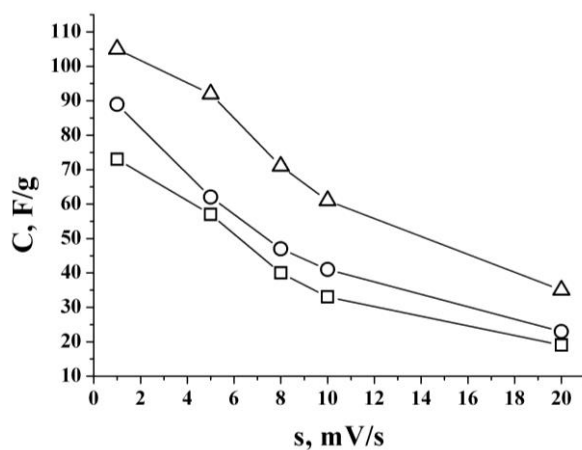


Fig. 6. Dependence of specific capacity of PCM in 0.5 M aqueous Solution of Li_2SO_4 – ■ -, Na_2SO_4 – ○ - and K_2SO_4 – on the scanning rate s

As is seen in the figure, the value of specific capacity decreases due to the increasing scanning rate. PCM in the aqueous salt solution of Li_2SO_4 has the lowest specific capacity and in aqueous K_2SO_4 the largest. This may be due to the fact that hydrated ions have different radius, i.e. Li^+ (3.82 Å), Na^+ (3.58 Å) and K^+ (3.31 Å), and different charge densities and movement rates [6, 10]. Based on the fact that the hydrated K^+ ions are the smallest and their ionic conductivity are the highest and movement time of hydrated K^+ ions along the pore is the shortest, it can be concluded that it is easier for them to achieve the internal pore of PCM than Na^+ and Li^+ . As a result, EC-based on aqueous solution of K_2SO_4 have the highest specific capacity at a high scanning rate. From the above it can be concluded that capacity increases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+$.

The investigated PCM was used to form EC-cases of standard size "2525". As an electrolyte we used 0.5 M aqueous solution of Li_2SO_4 , Na_2SO_4 and K_2SO_4 . Than we carried out measurements of capacity and internal resistance for EC.

A sharp voltage drop at a constant discharge current indicates the presence of internal resistance in EC. The technique consists in the oscillographic fixing of voltage drop (ΔU) of the capacitor at the time of its connection to a specific external resistance, and it is the closest method of practical application in EC internal resistance measurement. Fig. 7 shows the dependence of voltage drop of EC on the current applied.

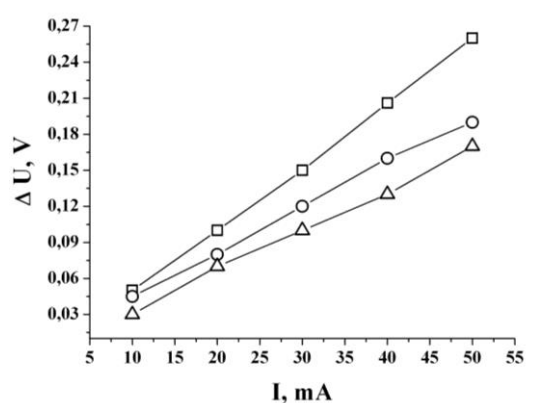


Fig. 7. Dependence of voltage drop of EC in 0.5M aqueous solution of Li_2SO_4 —■—, Na_2SO_4 —○— i K_2SO_4 —△— on discharge current

Specific capacity of samples was defined by using a galvanostatic method. The essence of this method is to determine the potential U depending on the time t at a constant current. As it can be seen in Fig. 8, for all the studied electrochemical systems capacity value decreases with the increase of discharge current. The maximum discharge current is 50 mA as further on its increase voltage drop exceeds 20 % of the maximum voltage during the discharge.

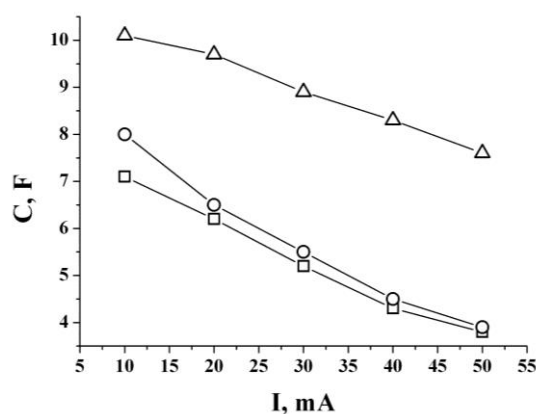


Fig. 8. Dependence of capacity of EC in 0,5M aqueous solution of Li_2SO_4 —■—, Na_2SO_4 —○— i K_2SO_4 —△— on discharge current

4. CONCLUSIONS

According to potential dynamic and galvanostatic studies it has been found that the specific capacity of carbon material depends on their electrochemically accessible surface area, involved in the formation of EDLC. The structure of carbon pores and molar ratio of the electrolyte are important factors that affect the value of capacity and total resistance of the electrochemical capacitor. It has been established that optimal is the use of 3M aqueous salt solution of Li_2SO_4 that provides specific capacity of carbon materials within $80\text{-}110\text{ F}\cdot\text{g}^{-1}$ at discharge current of $10\text{-}50\text{ mA}$.

We have studied electrochemical properties of PCM in 0.5 M aqueous solution of Li_2SO_4 , Na_2SO_4 and K_2SO_4 which showed that the velocity of hydrated ions in the bulk electrolyte and within internal pores of the electrode of PCM increases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+$, resulting in the improvement of PCM capacitive behavior in three electrolytes in the order $\text{Li}_2\text{SO}_4 < \text{Na}_2\text{SO}_4 < \text{K}_2\text{SO}_4$. Thus it is believed that for making a high power EC with and high energy density K^+ - and Na^+ -based aqueous electrolytes are more suitable than Li^+ -based electrolytes. The results obtained give valuable information for further study of new hybrid supercapacitors.

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Остафійчук Б.К., Будзуляк І.М., Рачій Б.І., Шийко Л.О., Лісовський Р.П., Іванічок Н.Я., Ващинський В.М. Вплив морфології поверхні на енергетичні характеристики нанопористих вуглецевих матеріалів. *Журнал Прикарпатського університету імені Василя Стефаника*, **1** (1) (2014), 17-25.

В даній роботі досліджено вплив морфології нанопористого вуглецевого матеріалу (НВМ) на його електрохімічну поведінку у водному електроліті. Встановлена оптимальна концентрація водного розчину сульфату літію, яка забезпечує максимальні питомі енергетичні характеристики конденсаторних систем типу C/Li₂SO₄/C. Проведені порівняльні дослідження ємнісних параметрів електрохімічних конденсаторів (ЕК) у водних розчинах сульфатів літію, натрію та калію різної молярності. Циклічні вольтамперограми при різних швидкостях сканування показують, що ємнісна поведінка НВМ в трьох електролітах покращується в порядку Li₂SO₄<Na₂SO₄<K₂SO₄. Це поліпшення може головним чином бути наслідком збільшення швидкості руху гідратованих іонів в об'ємі електроліту і у внутрішніх порах НВМ в порядку Li⁺<Na⁺<K⁺. Отримані результати дають цінну інформацію для вивчення нових гібридних суперконденсаторів.

Ключові слова: активований вуглецевий матеріал, подвійний електричний шар, електроліт, питома ємність, внутрішній опір, електрохімічний конденсатор.