

HYBRID ELECTROCHEMICAL SUPERCAPACITORS BASED ON AQUEOUS ELECTROLYTE SOLUTIONS

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Received 02.07.2012

In this paper it was investigated the system of the hybrid iodine electrochemical supercapacitor, which provides the discharge capacity over 7500 F/g. Microporous carbon material obtained by high temperature steam activation of the natural raw materials was used as an anode material for electrodes preparation. Moreover, the system of hybrid alkaline electrochemical supercapacitor was investigated, and it was proved, that additional activation of the activated carbon material in the molten NaOH can increase the available for charge surface of the material. As a result, discharge capacity per weight of active material can increase up to 342 F/g and the energy density is 6.5 times greater than value of known symmetric supercapacitors.

Keywords: ultracapacitor, electrochemistry, pseudocapacitance, activated carbon, hybrid supercapacitor.

В роботі використовуючи мікропористий вуглецевий матеріал, отриманий високотемпературною активацією у водяній парі природної сировини, досліджена система йодидного гібридного електрохімічного суперконденсатора, що забезпечує питому ємність на розряді понад 7500 Ф/г. Досліджена система лужного гібридного електрохімічного суперконденсатора і доведено, що доактивація активованого вуглецевого матеріалу в розплаві NaOH дозволяє підвищити доступну до заряду поверхню матеріалу. І як результат дозволяє підвищити розрядну ємність на масу активного матеріалу до 342 Ф/г та збільшує питому енергоємність в 6,5 разів у порівнянні з відомими симетричними суперконденсаторами.

Ключові слова: суперконденсатор, електрохімія, псевдоємність, активоване вугілля, гібридний іоністор.

В работе используя микропористый углеродный материал, полученный высокотемпературной активацией в водяном паре естественного сырья, исследована система йодидного гибридного электрохимического суперконденсатора, которая обеспечивает удельную емкость на разряде свыше 7500 Ф/г. Исследована система щелочного гибридного электрохимического суперконденсатора и доказано, что дополнительная активация активированного углеродного материала в расплаве NaOH, позволяет повысить доступную для заряда поверхность материала. И как результат позволяет повысить разрядную емкость на массу активного материала до 342 Ф/г и увеличивает удельную энергоёмность в 6,5 раз по сравнению с известными симметричными суперконденсаторами.

Ключевые слова: суперконденсатор, электрохимия, псевдоёмность, активированный уголь, гибридный ионистор.

INTRODUCTION

Electrochemical supercapacitors (SC) are power sources, which occupy an intermediate position between batteries and conventional capacitors. They are dynamically developing [2, 3] starting from the first patent for SC [1]. There are three main types of electrochemical supercapacitors:

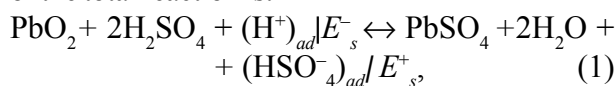
– double layer capacitors (DLC), which consist of ideally polarized electrodes (often from activated carbon) in organic and aqueous solutions of electrolytes [4];

– so-called pseudocapacitors, capacity of which is provided by a pseudocapacity of Faraday processes of polymers and metal oxides. For example, a pseudocapacity of hydrogenation-dehydrogenation of ruthenium oxides [5];

– hybrid electrochemical supercapacitors (HESC), which contain well polarized electrode, based on activated carbon material and almost unpolarized counter electrode in electrolyte systems. This allows to twice the growing of potential change of the carbon electrode and the

capacitance value of the unit, compared to the DLC, due to absence of the second serial polarized electrode in an equivalent electrical circuit. These factors can increase the energy of HESC some 2 to 5 times by comparison with the symmetrical design [6, 7].

However, existing electrochemical capacitor electrodes cannot provide capacity greater than 900 F/g, so it does not meet growing needs of various branches of engineering and automotive industry [4]. For example, if the HESC [6] is the system of not polarized electrode $\text{PbO}_2/\text{PbSO}_4$ and negative well polarized activated carbon electrode, between which the separator with an aqueous solution of sulfuric acid is located. In such system implementation of the total reaction is:



where E_s is surface of the electrode.

This system provides a capacitance of carbon electrode up to 600 F/g. The disadvantages of such systems are much smaller electrical capacities of the theoretically calculated for hybrid electrochemical capacitors, and low values of energy at considerable cost to the manufacture and using environmentally hazardous materials. Constantly growing demands of engineering and electronics can be satisfied only with much more power-consuming and more powerful devices with low cost and environmental cleanliness.

Objective of this paper is to create HESC with no polarized electrode and well polarized electrode based on activated carbon, which would provide tenfold increasing in electrical capacity, which would let increasing of the energy content, while using only environmentally friendly materials and lower cost of its production.

EXPERIMENTAL

Isotherms of the nitrogen adsorption were obtained by using Quantachrome NovaWin – Quantachrome Instruments (version 11.0). HESC have been jacketed into blister foil (fig. 1). They consist of polarized carbon electrode and unpolarized zinc-metal electrode divided by the separator with electrolyte and current collectors, which was made of stainless steel. The positive electrode was made from activated carbon with the addition of 3% teflon binder. It represents a square thin film, with 3 cm side, which thickness is 60 – 86 μm . For this purpose,

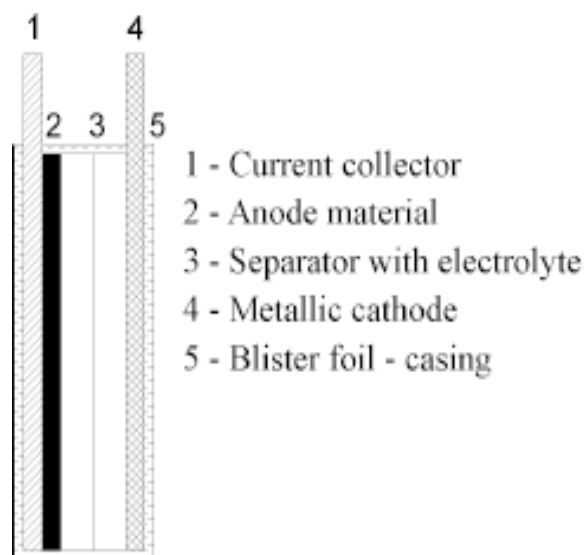


Fig. 1. Schematic structure of fabricated HESC prototype.

it was used activated carbon with the surface area 1246 – 1377 m^2/g . Coal film was pressed onto the current collector. Unpolarized electrode was made by prior electroplating of the metal onto the current collector with the layer thickness of 40 μm . Appointed electrodes was divided by a separator BAHYT-48 tacked in two layers, which was previously immersed in a water solution of 30% KOH or 20%LiI + 15%ZnCl₂. Charge and discharge characteristics were investigated with a help of AUTOLAB measuring complex made in Netherlands by “ECO CHEMIE”.

RESULTS AND DISCUSSION

Initial activated carbon material (ACM) was obtained by high temperature carbonization and activation of apricot seeds in water vapor at 950 °C. The BET surface area of material was 1246 m^2/g , according to nitrogen adsorption isotherms at 77 K (fig. 2a).

ACM was subjected to the activation in the melt of sodium hydroxide. Homogeneous mixture of material with fivefold weight of sodium hydroxide was heated in an atmosphere of argon from room temperature to 500 °C with speed of 20 °C per minute and it was held at this temperature for 30 min. Thus additionally activated material was washed in warm water from alkali and dried. The resulting activated material (ACMR) had a BET surface value equal to 1377 m^2/g (fig. 2b).

The resulting ACM was tested in the system of symmetric SC in aqueous 30% KOH. Galvanostatic charge-discharge results (fig. 3) was showed typi-

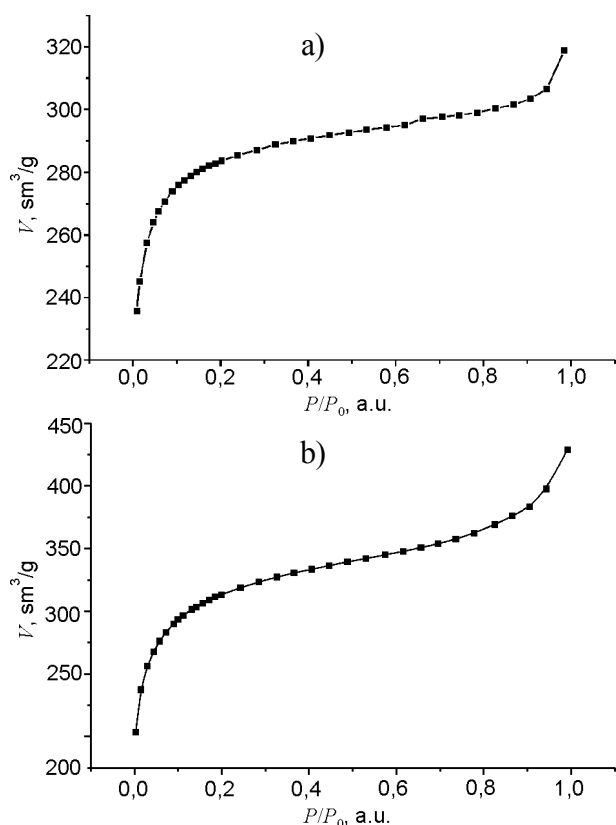
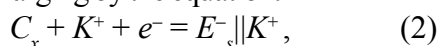


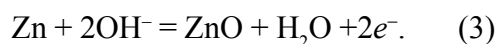
Fig. 2. Nitrogen adsorption isotherm for activated (a) and additionally activated in NaOH (b) carbon material.

cally high value of the coulomb cycle efficiency $\eta = 99\%$ and the capacitance $C = 186 \text{ F/g}$. According to the data represented in paper [8], it corresponds to $986 \text{ m}^2/\text{g}$ of available surface for potassium ions charging by the equation:



here C_x – surface of the porous structure of the ACM, K^+ – cations of the electrolyte, $||$ – dual layer, where charge is accumulated by the mechanism of physical adsorption.

The resulting value of $C = 186 \text{ F/g}$ is insufficient to build a competitive SC. Therefore, it was investigated the system of HESC, which contains positive polarized electrode based on ACMR and negative unpolarized zinc electrode, divided by a separator immersed in an aqueous 30% KOH. There is well reverse process (2) on the positive carbon electrode. And as well, reverse electrode process in alkaline medium of zinc-metal anode occurs on the negative electrode:



Thus the total reaction which is implemented in the capacitor will look like:

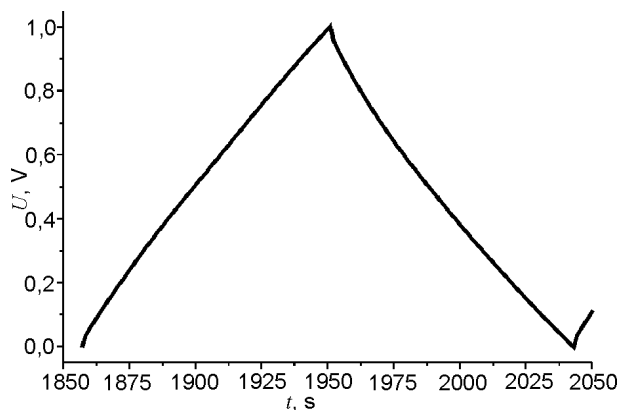
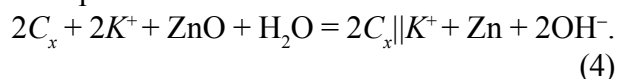


Fig. 3. Galvanostatic cycle of symmetric SC in 30% aqueous solution of KOH (current density is $i = 1 \text{ A/g}$).

Fig. 4 illustrates charge-discharge cycle of the proposed HESC. Cycle recorded in galvanostatic mode with current density $i = 1 \text{ A/g}$, which is calculated for an active mass of the working electrode. Discharge presented in fig. 4 is corresponding to the capacity $C = \Delta Q_d / \Delta U = 287 \text{ C/g} / 0.84 \text{ V} = 342 \text{ F/g}$ with a coulombic efficiency of the cycle $\eta = (\Delta Q_d / \Delta Q_c) \cdot 100\% = (287 / 290) \cdot 100\% = 99\%$, where $\Delta Q_d, \Delta Q_c$ – amount of charging and discharging electricity of the cycle. Significant increase in discharge capacity is related to increase of available for charge (by equation (2)) surface of ACMR up to $1100 \text{ m}^2/\text{g}$. Charging-discharging of ACMR is occurs in the electrode potentials from 0.04 to -0.9 V according to the standard hydrogen electrode.

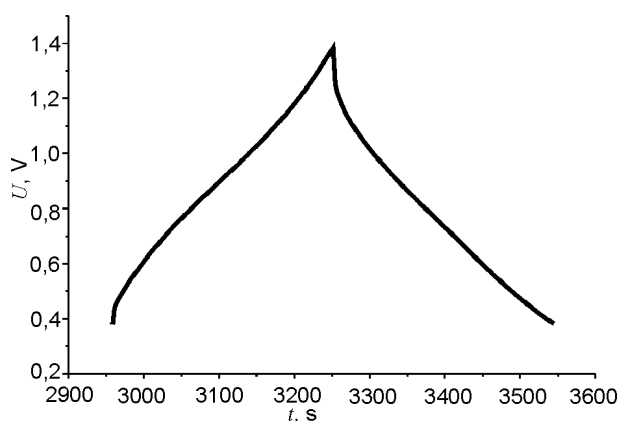


Fig. 4. The cycle of galvanostatic charge-discharge of proposed HESC with current density $i = 1 \text{ A/g}$.

Ragone dependence (fig. 5) has been calculated in the coordinates of energy density v . power density ($W-P$), submitted to the masses of both electrodes. For this, it was recorded galvanostatic cycles with different current loadings (from 1 to 5 A/g).

The discharge energy was determined by the equation:

$$W = \frac{C}{m_1 + m_2} \cdot \frac{U_2^2 - U_1^2}{2} = 311 \text{ F/g} \times$$

$$\times \frac{1.23^2 - 0.4^2}{2} \text{ V}^2 = 211 \text{ J/g} = 59 \text{ mW} \cdot \text{h/g}, \quad (5)$$

where C – capacity represented to the active mass of both electrodes (m_1 , m_2), U_2 and U_1 – voltage of beginning and expiration of the discharge, respectively. The power of discharge was determined according to the next equation: $P = i \cdot U_{avr} = 0.91 \text{ A/g} \times 0.82 \text{ V} = 0.74 \text{ W/g}$, here U_{avr} – discharge voltage, which corresponds to $0.5\Delta Q_d$. Coulombic efficiency of cycling was within 95 – 98%

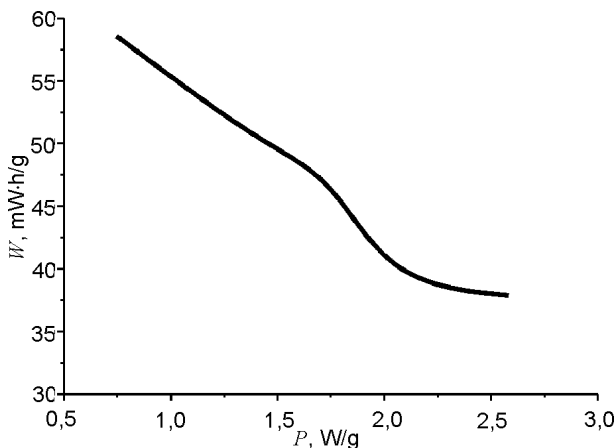
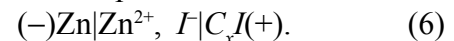


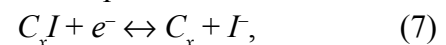
Fig. 5. Ragone dependence for investigated alkaline HESC.

The proposed alkaline HESC ensures 6.5 times increase at the energy obtained with a more than ninefold increase at the current load, compared to the alkaline symmetrical electrochemical supercapacitors [9 – 11]. For comparison of investigated energy storage systems with known lead acid and alkaline cadmium-nickel batteries, we assume that the proposed alkaline HESC will contain 30% by weight of active components of the cathode. That case values of the energy density and power density listed to the device will be $P = 222 \text{ W/kg}$ and $W = 18 \text{ W} \cdot \text{h/kg}$. Using data obtained from the high currents discharge [12] for lead battery ($P = 90 \text{ W/kg}$ and $W = 9 \text{ W} \cdot \text{h/kg}$) and for the cadmium-nickel batteries ($P = 200 \text{ W/kg}$ and $W = 10 \text{ W} \cdot \text{h/kg}$) we find, that the proposed HESC system shows double increase of both parameters compared to the lead battery, and shows an 1.8 times increase in the energy intensity with simultaneously little power increase, with the comparison to the cadmium-nickel battery.

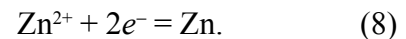
The ability of microporous activated carbon materials to charge up to 2000 F/g at the positive electrode polarization, which does not reach the potential of iodine allocation in the free state, has been shown in articles [13, 14]. Therefore, this article investigates iodine HESC, which has polarized, on the basis of ACM with $S = 1246 \text{ m}^2/\text{g}$, and unpolarized metal electrodes, between which the separator with 20%LiI + 15%ZnCl₂ dissolved in water is located. Consideration of the most well-known from the literature values for iodine index of activated carbon materials – 1.1 mg/m², and the electrochemical equivalent of iodine $13.16 \cdot 10^{-4} \text{ g/C}$, we have calculated the maximum electric charge of the surface by iodine atoms – $q_I = 0.836 \text{ C/m}^2$. In this case, the maximum calculated electric charge for our investigational ACM is $C = 0.836 \text{ C/m}^2 \times 1246 \text{ m}^2/\text{g} = 1042 \text{ C/g}$. Metallic zinc was used as an unpolarized electrode material. The system of iodine HESC can be represented as follows:



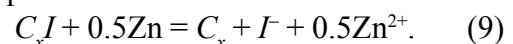
Well reverse process of electrochemical intercalation of ions into the pores with diameter $d \geq 0.45 \text{ nm}$ occurs at polarized carbon electrodes:



where $x = 9$. Process of electrolytic deposition and anodic dissolution of metal is occurs at unpolarized electrode:



Overall current creative process of iodine HESC can be represented as follows:



Manufactured HESC was charged in the potentiostatic mode at the potential of 1.25 V for two hours and discharged in the galvanostatic mode with value of current density – 480 mA/g (fig. 6).

The resulting value of capacitance is equal to $C = 834.75 \text{ C/g}/0.11 \text{ V} = 7589 \text{ F/g}$, which is calculated to the polarized electrode active material, which is 12,8 times greater than the maximum capacity of carbon electrode reported in the literature [6]. The discharge capacity and the electrical capacity of iodine HESC (fig. 6) values was $P = 420 \text{ W}$ and $W = 214 \text{ W} \cdot \text{h}$ per 1 kg of active mass of used electrodes. Assume that the proposed iodine HESC will contain 25% by weight of active components of the cathode, for comparison investigated system of iodine HESC with known lead acid batteries and alkaline cadmium-nickel batteries.

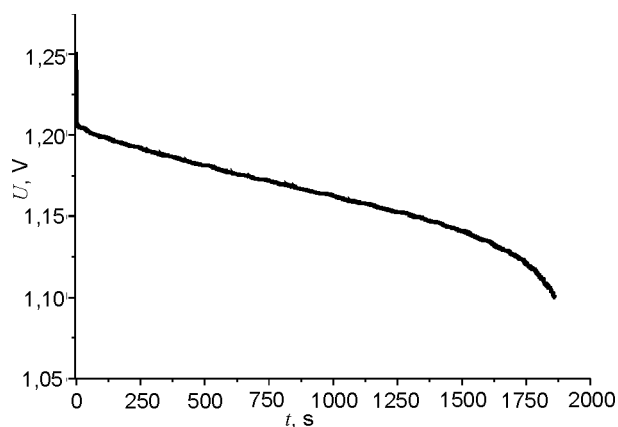


Fig. 6. Galvanostatic discharge of iodine HESC with current density 480 mA/g.

Then the value of these physical quantities at device will be $P = 105$ W/kg and $W = 53.5$ W·h/kg, which is 6 times higher than energy consumption of lead battery with comparable power.

CONCLUSIONS

1. High temperature activation of apricot seeds in water vapor provides a microporous activated carbon material with the surface by BET equal to 1246 m²/g, and its further activation at melted NaOH increases the specific surface area to 1377 m²/g.
2. Using additionally activated carbon material in the system of alkaline hybrid electrochemical supercapacitor provide 6.5 times increasing of the energy obtained in more than ninefold increase in the current load, in comparison with alkaline symmetrical electrochemical supercapacitors.
3. As cathode component of the iodine hybrid electrochemical supercapacitor investigated activated carbon material provides capacity that is 12.8 times exceeds the maximum capacity of carbon electrodes, which was reported in literature. Obtained values of discharge power and electrical capacity for this system reached $P = 420$ W and $W = 214$ W·h per 1 kg of active mass of used electrodes.
4. There are perspective of design and technological work to create the appropriate device, because comparing the discharge characteristics of the investigated hybrid electrochemical supercapacitors with lead acid battery show the predominance of the first.

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