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DEVELOPING OF HYBRID ELECTRODES FOR SUPERCAPACITORS FROM BIOMASS-DERIVED ACTIVATED CARBONS WITH CARBON NANOTUBES

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Abstract

In this paper, environmental clean, activated carbons (AC) and flexible, long, conductive FWCNT (Few walled carbon nanotubes) were used as a composite material to create a hybrid supercapacitor electrode without addition of polymer binder materials. In work to create electrode, an activated carbons (AC) was used, which was obtained from walnut shell (WS), apricot stones (AS) and activated carbon of brand YP-80F (Kuraray Chemical Co., Osaka Japan) and FWCNT, in weight ratio AC:FWCNT 9:1. The strong hybrid electrodes AC-FWCNT were obtained by a light three-step method (mixing, dispersion and filtration). Electrochemical properties of the obtained electrodes were investigated by the method of Cyclic Voltammetry (CV). Also, the morphological properties of the obtained electrodes were studied by the Scanning Electron Microscope (SEM), the specific surface by the Brunauer-Emmett-Teller analysis. Based on the results of a study of the electrochemical characteristics of electrodes based on carbon materials, the AS-FWCNT, WS-FWCNT hybrid electrodes showed a high specific capacity than the YP-80F-FWCNT electrodes.

Keywords: electrochemical capacitors, electrode, activated carbons, few-walled carbon nanotubes

Introduction

Electrochemical capacitors, which known as supercapacitors, are a unique type of high-power devices being developed for a different type of applications as consumer electronics, medical devices, transportation and military defense systems. However, electrochemical characteristics as energy and power densities, ecologically friendliness and cycle life, also cost of supercapacitors need to be significantly improved to fulfill the dramatically increasing performance needed for different applications. Thus, the development of new electrochemical electrodes with high performances is important [1].

Nowadays, the demand for clean, sustainable energy sources is very high. Activated carbon (AC) is a porous material with high surface area and can exhibit good adsorptive capacities. The high specific surface area (SSA) of 1000-3500 m^2g^{-1} and the porous structure of AC let charge storage at the electrode/electrolyte interaction, the capacitance of mentioned interaction is equal to 10 $\mu F\ cm^{-2}$ [2]. Activated carbon can be synthesized from vegetable raw materials as apricot stone, rice husk, coconut shell, walnut shell.

Organic based carbonaceous materials one of the most widely used raw materials for electrodes [3] because of low cost and easy to fabricate. In this paper, we used activated carbons obtained from rice husk and apricot stones which are waste of agricultural industry. For example, production of rice husk consist about 545 million tons per year. Rice husk (RH) and apricot stones (AS), walnut shell consists of a number of organic compounds, the main ones being cellulose, hemicellulose lignin and amorphous silicon dioxide. The RH contain 35% of carbon and about 15-20% of silicon dioxide. Accordingly, the methods of development of biomass-derived activated carbons are ecologically friendly which is very important. The development of technologies for the production of electrodes for electrochemical capacitors based on the use of agricultural waste is economically and technologically justified direction [4, 5]. Obtaining of activated carbons from RH and AS can solve two environmental problems: utilization of an agricultural waste into a material with high surface area for electrodes of electrochemical storage devices.

Another group of carbon materials which can be used in supercapacitor electrodes are carbon nanotubes. Carbon nanotubes have properties as tensile strength, flexibility, electrical conductivity and high specific surface area. High conductivity and high surface area range are critical to the construction of electrochemical electrodes. CNTs have also been used in electrode as current-collecting substrates in addition with conductive polymers and metal oxides [6, 7]. Application of SWCNTs at electrochemical electrodes have advantages as good electric conductivity, large surface area about 1320 m^2 g^{-1}. At pure SWCNT electrodes show high performance, but their cost up to 1000 USD per g^{-1}. Nevertheless, SWCNTs aggregate and form disordered structure which will interfere to show their normal mechanical and electronic properties. It occurs due to van der Waals interactions in SWCNTs. In the case of MWCNT, there are some problems as less conductivity and insufficient surface area (~300 m^2/g), but MWCNTs are cheaper than SWCNTs [8, 9].

In 10, 11 was synthesized few-wall CNTs (FWCNTs). Difference of FWCNTs from SWCNTs are low cost, high electronic conductivity (~100 S/cm) because of long length (~400 μm) and ease to manipulation.

Preparation of electrodes from CNTs with AC in hybrid electrodes has been developed to improve electrical conductivity of common electrodes, and to replace ordinary conductive additives. It is desirable to combine the high surface area of ACs with the conductivity of CNTs to obtain an electrode with enhanced capacitive performance as high electrolyte-accessibility. The methods of obtaining films of AC and FWCNTs have been studied, and these electrode materials show high-capacity without using metal collectors, which leads to decreasing of weight of the fabricated device.

In this study, capacitive AC particles obtained from waste of agricultural industry WS and AS at the Institute of Combustion Problems in the Laboratory of Carbon Nanomaterials and Nanobiotechnologies, were integrated with conductive, flexible FWCNT to fabricate conductive electrodes with high-electrochemical capacity. The electrochemical characteristics of AS-FWCNT, WS-FWCNT hybrid electrodes were compared with YP-80F-FWCNT (Kuraray Chemical Co., Osaka, Japan) electrodes. The electrodes were investigated by full-type configuration with Ti mesh to evaluate the performance of hybrid electrodes. It is clear that the ultimate characteristics of carbon-based electrochemical capacitors will be closely linked to the physical and chemical properties of the electrodes.

Experimental part

All AC samples were sieved by AS ONE MVS-1 sieve. Sieve has 3 parts with different size: 75 μm, 53 μm, 25 μm and it has a mode of controllable automatic shaking. After sieving, samples of ACs (WS, AS) separated by different size: > 100 μm, 100-75 μm, 75-53 μm, 53-25 μm, < 25 μm.

To prepare AC-FWCNT hybrid electrodes, 0.5 mg of FWCNTs were mixed with YP-80F activated carbon for supercapacitors (5-20 μm diameter, 1900-2200 m^2g^{-1}), activated carbons which was obtained from apricot stones, walnut shell in AC:FWCNT weight ratios of 9:1. Both carbon materials were added to ethanol (EtOH) and dispersed in a bath-type sonicator with a cooling unit to keep the temperature at 20 ^{0}C. At work [12] EtOH was selected as solvent for the dispersion of carbon materials, because of its ease of working, good compatibility with carbon materials. Also it is easy to remove EtOH from pores of hybrid electrodes through drying. The electrodes were obtained by vacuum filtration over polytetrafluoroethylene (PTFE) membrane filters (5 μm pore size). The final product was a mechanically-robust matrix of interwoven FWCNTs that held the YP-80F, AS, WS. Residual solvent was removed by drying at 90 ^{0}C for 2 hours.

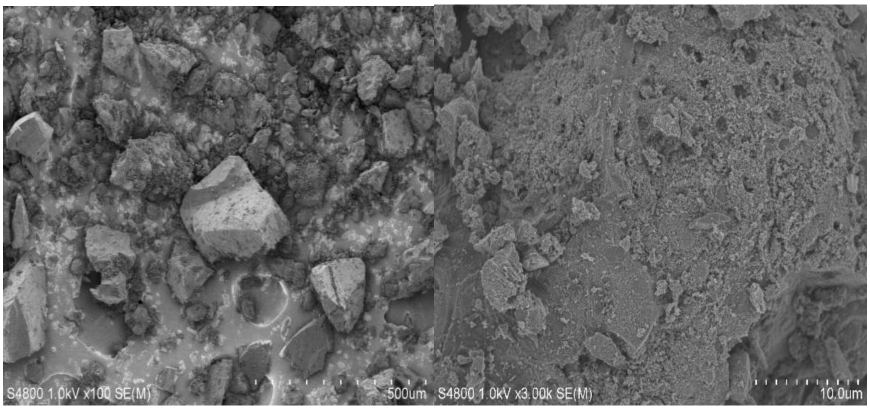
Microstructures of the AC-FWCNT based films were analysed by scanning electron microscopy (SEM, Hitachi S-4800, Tokyo, Japan). SSAs were calculated by Brunauer-Emmett-Teller (BET) analysis of nitrogen absorption isotherms measured at 77 K (BEL Japan Belsorp-28SA, Osaka, Japan).

To evaluate the performance of the FWCNT 3D collector matrix, Ti-mesh (200 L *200 S) connected to the carbon electrodes were prepared. Electrode cells were used to run cyclic voltammetry.

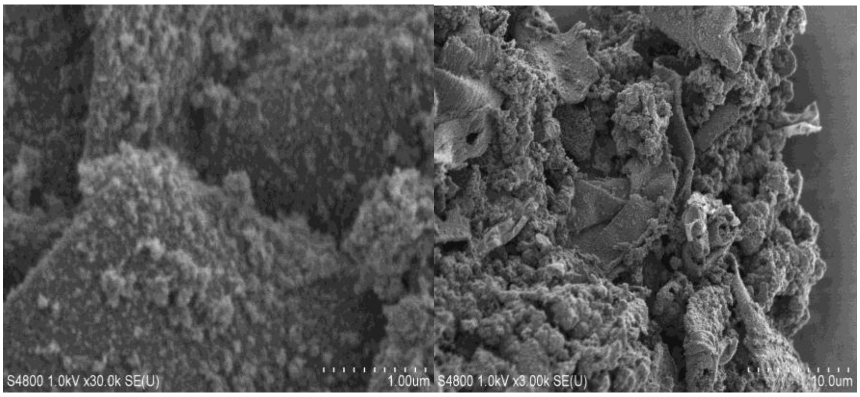
The three-electrode cell consisted of an YP80F-FWCNT, AS-FWCNT, WS-FWCNT as a working electrode, a YP-80F-FWCNT counter electrode and a Ag/AgCl electrode (in saturated NaCl aqueous solution) reference electrode; the electrolyte was 1M Na_2SO_4 aqueous solution.

Results and discussion

The morphological features of activated carbon samples obtained from rice husk, apricot stones, walnut shell were observed by SEM (Figure 1). As can be seen from Figure 2, the ACs have a porous, rough structure and contain particles of different diameters. The distribution of AS, WS particle size is large. Powder of activated carbon obtained from AS contain some particles with diameter larger than 250 μm, RH about 500 μm and also particles with smaller diameter. For the capacitive particles, their particle diameter is crucially important because FWCNT matrix cannot support the electrical conduction within each capacitive particle. In case of AC particles, the effect of their size is carefully assessed. In work [12] specific capacitance of hybrid electrodes made with different size of activated carbons was compared. The hybrid electrodes with smaller particles show higher specific capacitance and rate performance than electrodes with larger one. Also Zhang et al [13] investigated effect of particle size of activated carbon with high surface area and they have found that using of smaller AC particles for hybrid electrodes are effective at enhancing the rate performance. It is due to low resistivity of between particles and rapid diffusion of ions within pores of AC particles. Accordingly, AS and WS particles were separated by size to form flexible, hybrid electrodes with FWCNT.



a



b

a – obtained from AS, c – WS

Fig.1 – SEM images of ACs

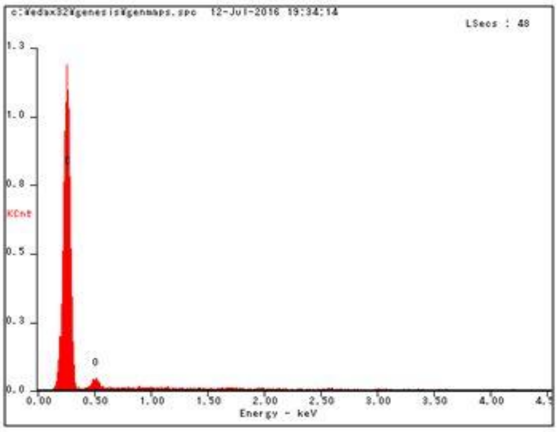
To study elemental composition of ACs were carried out EDAX analysis of samples. As shown from EDAX analysis (Figure 2) ACs obtained from apricot stones, walnut shells contain carbon and oxygen atoms.

Table 1 shows activation methods and specific surface area of ACs. AC obtained from WS shows highest specific surface area about 2552 m^2/g.

Preparation of electrodes from CNTs with AC in hybrid electrodes has been developed to improve electrical conductivity of common electrodes, and to replace ordinary conductive additives. It is desirable to combine the high surface area of ACs with the conductivity of CNTs to obtain an electrode with enhanced capacitive performance as high electrolyte-accessibility.

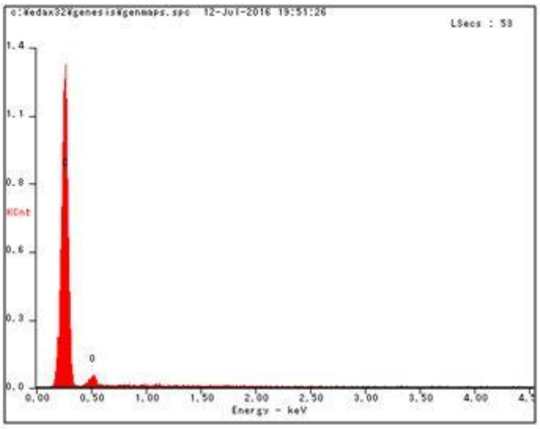
Table 1 – Methods of activation and specific surface area of ACs

AC	Type of raw materials	Activation method	Specific surface area, m^2/g
AS	Apricot stones	H_3PO_4 (70%)	2030
WS	Walnut shell	H_3PO_4 (70%)	2552
YP-80F	Coconut shell	steam	2200



Element	Wt%	At%
CK	92.98	94.64
OK	7.02	5.36
Matrix	Correction	ZAF

a



Element	Wt%	At%
CK	92.69	94.41
OK	7.31	5.59
Matrix	Correction	ZAF

b

Fig.2 – EDAX-analysis of activated carbons obtained from AS (a) and WS (b)

The methods of obtaining films of AC and FWCNTs had been studied at [12, 13], and these electrode materials show high-capacity without using metal collectors, which leads to decreasing of weight of the fabricated device. AS-FWCNT, WS-FWCNT hybrid electrodes are prepared without using binders and it has self-supporting flexible nature (Figure 3c). The morphological features of electrodes are given at Figure 3. The Figure 3 (a, b) shows uniformly distribution of AS, WS particles and covering with FWCNT. The long flexible FWCNTs wrap around AS, WS particles, which would not be possible with conductive materials.

The results of electrochemical measurements were obtained from CV tests in a three-electrode cell in the range -1–0.6 V vs. Ag/AgCl, using the full-contact Ti-mesh configuration.

The specific capacitance was calculated from the CV plots using the expression:

$$C = \frac{q}{\nu} = \frac{1}{\nu}\frac{\int_{E_1}^{E_2} i(E)dE}{E_2 - E_1} \qquad (1)$$

where C is capacitance, q is electric charge, ν is the scan rate, E is voltage and i is current. The mass of AC, AS was used in the capacitance calculation [12].

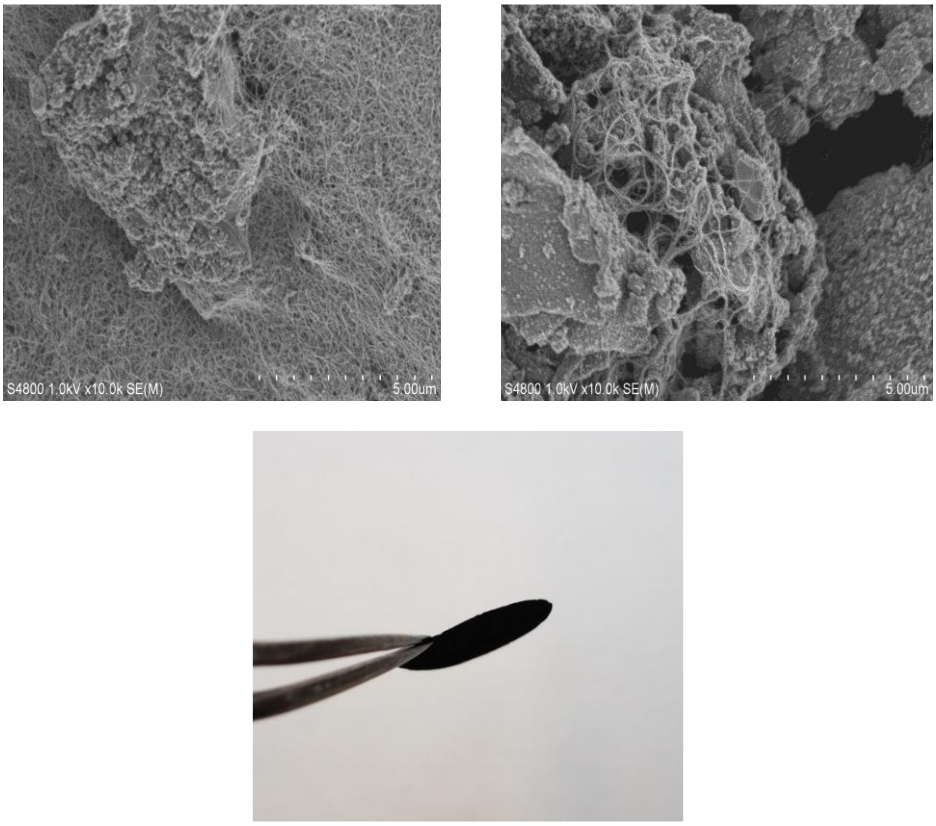


Fig. 3 – Morphology of a typical AC-FWCNT electrode: (a and b) SEM images and (c) photograph

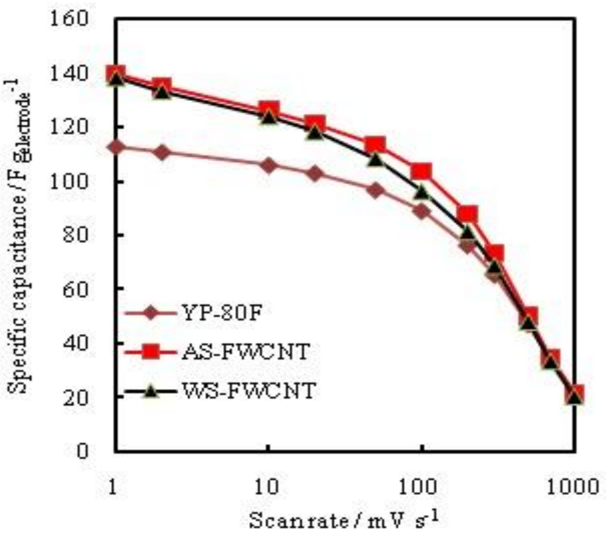
Specific capacitance of hybrid electrodes collected with different size of AS particles presented in Figure 4a. An increase of specific capacitance was observed for the AS-FWCNT and WS-FWCNT hybrid electrodes. Hybrid electrode which were made with YP-80F particles show lower rate performance than other electrodes. The maximum specific capacitance of AS-FWCNT was 140 F/g and WS-FWCNT was 138 F/g, while the specific capacitance of the standard electrode YP-80F-FWCNT was equal to 106 F/g. The AS-FWCNT has a specific capacitance of 132 and 104 F/g, WS-FWCNT 130 and 96 F/g with a scan rate of 5 and 100 mV/s, which indicates a significant difference in electrochemical characteristics, compared to the hybrid electrodes YP-80F-FWCNT.

Figure 4b shows CV curve of hybrid electrodes AS-FWCNT, RH-FWCNT, YP-80F-FWCNT. The CV curve of the hybrid electrodes has a rectangular shape, which indicates the property of the capacity of the double layer. CV curve shows a wide peak of oxidation and reduction, which appears due to rapid redox reaction. Redox peak sources can be associated with the release and adsorption of activated oxide groups on the surface of the carbon electrode and the subsequent formation of quinone groups [14]. A higher capacity at low scanning speeds is typical for porous electrodes. With a faster scanning speed, fewer pores contribute to the specific capacitance, since ion motion occurs faster and the available surface area is not large [15].

It is generally accepted that carbon materials with a high specific surface area can display a high specific capacity, since there is more space for accumulating charge and forming an electrical double layer. However, as we can see from the obtained results other important factors, such as electrical conductivity, pore distribution, electrolyte type and surface chemistry, play an important role in the specific capacity of the material, and the ratio between specific capacity and surface area is not linear.

Conclusion

We obtained self-supporting carbon hybrid electrodes by enclosing highly-capacitive activated carbon particles within an electrically conductive 3D collector made of FWCNTs. Hybrid electrodes were prepared from biomass derived ACs obtained from apricot stones and walnut shells with sub-millimeter long FWCNTs.



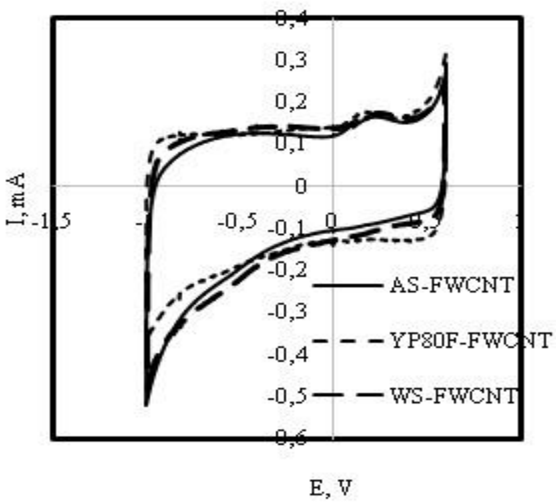


Fig. 4 – Electrochemical characterization of AC-FWCNT hybrid electrodes

The FWCNTs provides mechanical stability and fewer contact and junction resistances, making it possible to produce self-supporting electrodes with no additional binder materials. The fabrication method followed in this work can rapidly and easily produce lightweight electrodes with controlled thicknesses for varied applications, given its important advantage over other, more complicated procedures.

References

[1] Wen Lu, Rachel Hartman. Nanocomposite Electrodes for High-Performance Supercapacitors // J.Phys.Chem.Lett. – 2011. – V.2. –p.655-660.

[2] A. Lewandowski and M. Galinski. Practical and theoretical limits for electrochemical double-layer capacitors // J. Power Sources. -2007. – №173., -p.822.

[3] Nirwan Syarif. Performance of Biocarbon Based Electrodes for Electrochemical Capacitor // Energy Procedia. -2014. – V.52. - p. 18-25.

[4] K.K. Kudaybergenov, E.K. Ongarbayev, Z.A. Mansurov. Thermally treated rice husks for petroleum adsorption // International Journal of Biology and Chemistry. –2012. –V.3. -p. 3-12.

[5] A.R. Kerimkulova, M.A. Seitzhanova, M.R. Kerimkulova, M.Zh. Mambetova, Z.A. Mansurov. Preparation of activated carbons using carbonation rice husks, poplar tree, saxaul, corncob and apricot stones // News of the National Academy of Sciences of the Republic of Kazakhstan, Series chemistry and technology. -2015. – №.3 (411) - p. 67 – 77.

[6] Y. Honda, T. Haramoto, M. Takeshige, H. Shiozaki, T. Kitamura, K. Yoshikawa and M. Ishikawa. Curvature effects in carbon nanomaterials: Exohedral versus endohedral supercapacitors // J. Electrochem. Soc. – 2008. – V.155 –p.930.

[7] C. Niu, E. K. Sichel, R. Hoch, D. Moy and H. Tennent. High power electrochemical capacitors based on carbon nanotube electrodes // Appl. Phys. Lett. –1997. –V.70. -p. 1480.

[8] L. A. Girifalco, M. Hodak and R. S. Lee, Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential // Phys. Rev. B: Condens.Matter. – 2000. –V.62. –p.13104.

[9] T. Hertel, R. E. Walkup and P. Avouris. Deformation of carbon nanotubes by surface van der Waals forces // Phys. Rev. B: Condens. Matter. -1998. –V.58. –p.13870.

[10] Kim D. Y., Sugime H., Hasegawa K., Osawa T., Noda S. Sub-millimeter-long carbon nanotubes repeatedly grown on and separated from ceramic beads in a single fluidized bed reactor // Carbon. -49. -2011. –P.1972.

[11] Chen Z., Kim D. Y., Hasegawa K., Osawa T. and Noda S. Over 99.6 wt%-pure, sub-millimeter-long carbon nanotubes realized by fluidized-bed with careful control of the catalyst and carbon feeds // Carbon.- 2014. -80. –P.339.

[12] Ricardo Quintero, Dong Young Kim, Kei Hasegawa, Yuki Yamada, Atsuo Yamada and Suguru Noda. Important factors for effective use of carbon nanotube matrices in electrochemical

capacitor hybrid electrodes without binding additives // RSC Adv. -2015. – V.5. –P.16101.

[13] Zhang L.L., Zhou R. and Zhao X.S. Graphene-based materials as supercapacitor electrodes // J. Mater. Chem. -2010, -V.20, -P.5983.

[14] Kim K.-W., Kuppuswamy M. and Savinell R.F. Electrochemical oxidation of benzene at a glassy carbon electrode // J. Appl. Electrochem. -2000. –V.30, P.543–549.

[15] Quintero R., Kim D. Y., Hasegawa K., Yamada Y., Yamada A. and Noda S. Carbon nanotube 3D current collectors for lightweight, high performance and low cost supercapacitor electrodes // RSC Adv. -2014. -V. 4, -P.8230.

РАЗРАБОТКА ГИБРИДНЫХ ЭЛЕКТРОДОВ СУПЕРКОНДЕНСАТОРА ИЗ АКТИВИРОВАННЫХ УГЛЕРОДОВ ПОЛУЧЕННЫХ ИЗ БИОЛОГИЧЕСКОГО СЫРЬЯ С УГЛЕРОДНЫМИ НАНОТРУБАМИ

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Аннотация

В данной работе экологический чистый, полученный из отходов растительного сырья активированные угли (АУ) и гибкий, длинный, проводящий FWCNT (Few walled carbon nanotubes) применялись в качестве композитного материала для создания гибридного электрода суперконденсатора без добавления полимерных связующих материалов. В работе для создания электрода применяли АУ полученный из скорлупа греческого ореха (ГО), абрикосовой косточки (АК) и активированного угля марки YP-80F (Kuraray Chemical Co., Osaka Japan) и FWCNT, соотношение АУ:FWCNT 9:1. Прочные гибридные электроды АУ-FWCNT были получены легким трехступенчатым методом (перемешивание, дисперсия и фильтрация). Электрохимические свойства полученных электродов были исследованы методом Циклической Вольтамперометрии (ЦВ). А также, морфологические свойства полученных электродов была исследована Сканирующим электронным микроскопом (СЭМ), удельная поверхность – анализом БЭТ. По результатам исследовании электрохимических характеристик электродов на основе углеродных материалов, гибридный электрод AS-FWCNT, WS-FWCNT показала высокую удельную емкость YP-80F-FWCNT электроды.

Ключевые слова: электрохимический конденсатор, электрод, активированный углерод, углеродная нанотрубка с несколькими стенами

СУПЕРКОНДЕНСАТОРҒА БИОЛОГИЯЛЫҚ ШИКІЗАТТАН АЛЫНҒАН АКТИВТЕЛГЕН КӨМІРСУТЕКТЕР МЕН КӨМІРТЕКТІ НАНОТҮТІКШЕЛЕРДЕН ГИБРИДТІ ЭЛЕКТРОД АЛУ

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Аннотация

Берілген жұмыста экологиялық таза, өсімдік шикізаты қалдықтарынан алынған активтелген көміртектер (АС) және икемді, ұзын, өткізгіш FWCNT (Few walled carbon nanotubes), полимер байланыстырғыш материалын қолданбай суперконденсатордың гибридті электродын алу үшін қолданылды. Жұмыста электрод алу үшін грек жаңғағы қабықшасынан (WS), өрік сүйегінен (AS) алынған және YP-80F маркалы активтелген көміртек пен FWCNT 9:1 қатынаста қолданылды. Мықты гибридті электродтар AC-FWCNT жеңіл ушсатылы әдіспен (араластыру, дисперсия, фильтрлеу) алынды. Алынған электродтың электрохимиялық қасиеттері циклді вольтамперометрия әдісімен зерттелді. Сонымен қатар, алынған электродтардың морфологиялық қасиеттері сканирлеуші электронды микроскоппен (СЭМ), меншікті беттік аудан БЭТ анализ арқылы зерттелінді. Көміртекті наноматериалдар негізіндегі электродтардың электрохимиялық қасиеттерін зерттеу натижесінде AS-FWCNT, WS-FWCNT гибридті электроды YP-80F-FWCNT электродына қарағанда жоғары меншікті беттік аудан көрсетті.

Түйінді сөздер: электрохимиялық конденсатор, электрод, активтелген көміртек, бірнеше қабатты көміртекті нанотүтікше