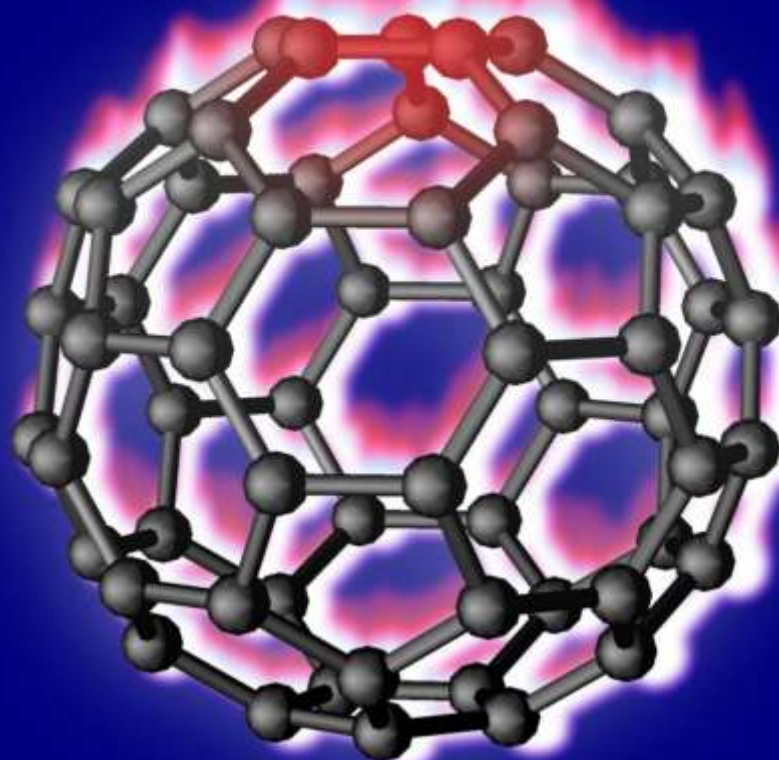


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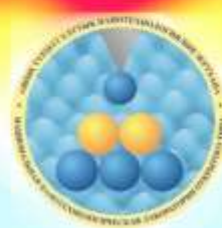
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Chapter 5

ORAL PRESENTATIONS

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TABLE of CONTENTS

Harris P., Electron Microscopy Laboratory, Department of Chemistry, University of Reading, UK	2
Structural transformation of graphite by passage of an electric current	
Teltayev B.B., Almaty, Kazakhstan	6
Increasing of low temperature stability of bitumen with the use of nanocarbon powder	
Ongarbayev EK, Almaty, Kazakhstan	10
Removal of metals and sulfur from tar by adsorbents modified with rare metals and nanocarbon	
Abdulkarimova R.G., Almaty, Kazakhstan	14
Self-propagating high temperature synthesis of composite materials based on boron carbide	
Sultanov F.R., Almaty, Kazakhstan	17
Recent developments in oil/water separation techniques	
Suleimenov K.A., Astana, Kazakhstan	21
Study of thermooxidative pyrolysis of Shubarkol coal in a circulating fluidized layer	
Nurpeissova A., Astana, Kazakhstan	25
Novel Li ₄ Ti ₅ O ₁₂ /Si/C-PAN composite anode for lithium-ion batteries	
Azat S., Almaty, Kazakhstan	26
Silica/Ag composite materials as a new adsorbent for the removal of mercury ions from water	
Temirgaliyeva T.S., KazNU, Almaty Kazakhstan	29
Effective use of Carbon nanotube matrices in high-performance, lightweight electrochemical capacitor electrodes	
Medyanova B.S., Almaty, Kazakhstan	33
Synthesis of carbon nanostructures by the method of low-temperature CVD in the presence of electric field	
Seitzhanova M., Almaty, Kazakhstan	37
Obtaining graphene-based membranes	

EFFECTIVE USE OF CARBON NANOTUBE MATRICES IN HIGH-PERFORMANCE, LIGHTWEIGHT ELECTROCHEMICAL CAPACITOR ELECTRODES

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Abstract. This paper presents the results of effective use of carbon nanotube matrices with activated carbon in high-performance, lightweight electrochemical capacitor electrodes.

Introduction

The storage of electrical energy has become one of the fundamental enablers for the technologically rich society of the 21st Century. It seems electrical energy storage may be even more important for the developments and directions of human civilization in the future. Nowadays manufacturing and transportation activities depend on the combustion of fossil fuels. As we know these fuels are non-renewable, due to this environment-friendly and fuel efficient systems are the aim of many researches. Electrochemical energy storage is fundamental in those energy systems and devices with defined mechanisms and structure are commercially available for various applications [1].

Nowadays, activated carbons widely used as main material for ECs electrode, because of their high SSA and reasonable cost. Activated carbons can be obtained from carbon-rich organic precursors by carbonization (heat treatment) in inert atmosphere with following activation processes as oxidation in CO₂, water vapour or KOH to increase the SSA and pore volume. Natural materials, such as coconut shells, wood, pitch or coal, apricot stones, walnut shell [2] rice husk or synthetic materials, such as polymers, can be used as precursors [3].

Another group of carbon materials which can be used in supercapacitor electrodes are carbon nanotubes. Carbon nanotubes (CNTs) possess high tensile strength, exibility, electrical conductivity and reasonably high SSA. Single-wall CNTs (SWCNTs) have the highest SSA for their exterior surface among CNTs, of up to 1320 m²g⁻¹. Pure SWCNT electrodes exhibit excellent rate performance, although their cost of up to 1000 USD per g limits their practical application. CNTs have also been used in electrodes as current-collecting substrates for other active materials such as conductive polymers and metal oxides, and with high-voltage window electrolytes. However, the strong van der Waals interactions in SWCNTs leads to formation of bundles and disordered networks, which makes it difficult to realize their optimum mechanical and electronic properties [4,5].

In [6] 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.

Combining CNTs with AC in hybrid electrodes has been explored to increase the conductivity of conventional electrodes, and as a replacement for conventional conductive additives. Self-supporting hybrid films of AC and CNTs have been reported, [7,8] which may produce light-weight, high capacity electrodes without using metal collectors, thus avoiding their contribution to the weight of the device.

Experimental part

To prepare AC-FWCNT hybrid electrodes, 0.5 mg of FWCNTs were mixed with WS (walnut shell) activated carbon for supercapacitors ($2552 \text{ m}^2\text{g}^{-1}$), activated carbons which was obtained from 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°C . At work [7] 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 ($5 \mu\text{m}$ pore size). The final product was a mechanically-robust matrix of interwoven FWCNTs that held the WS. Residual solvent was removed by drying at 90°C for 2 hours.

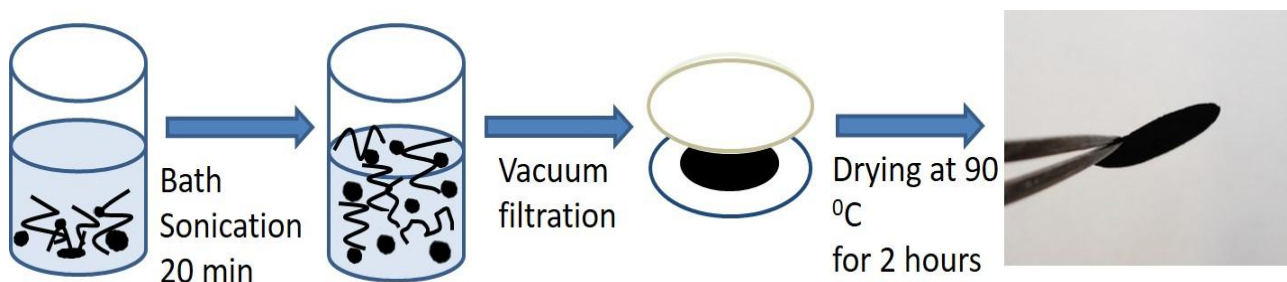
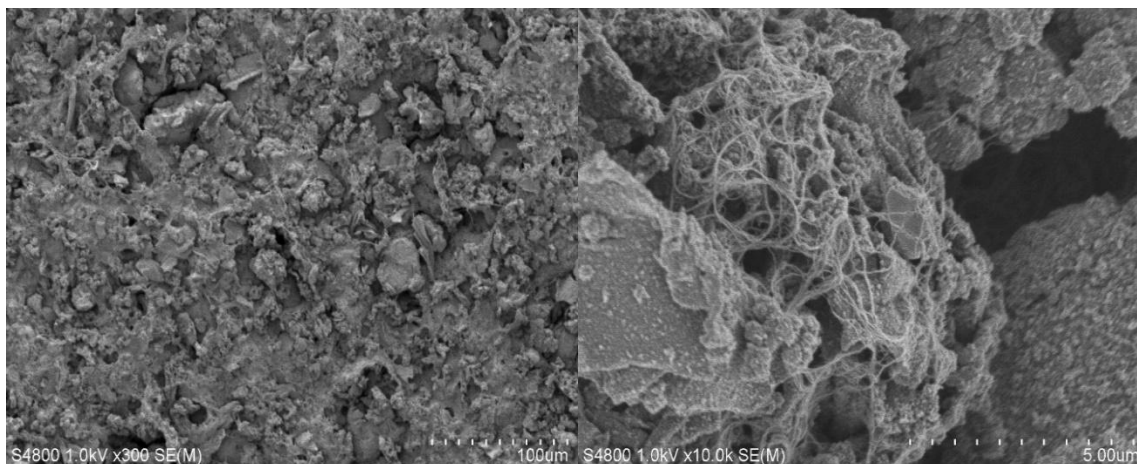


Figure 1. Scheme of electrode preparation

Results

The figure shows the SEM images of the sample WS-FWCNT at 300 (a) and 10,000 (b) times. The obtained electrode has a developed porous structure with a plurality of cells and voids. Carbon nanotubes covered the surface of activated carbon particles thereby facilitating the creation of self-supporting films of the WS-FWCNT.

The specific surface area, structure and capacitance values for the WS-FWCNT hybrid films are summarized in Table 1. As can be seen from the measurements, the specific surface area of papers increase with decrease of particle size of activated carbons. But with the change in size of the activated carbon particles obtained from the walnut shell, the specific capacity of the hybrid electrode does not change. The maximum specific capacity in 1 mV/s was reached when was used WS particles between $75\sim 100 \mu\text{m}$. Also the volumetric and areal capacitance were calculated to the WS-FWCNT hybrid electrodes. As can be seen from Table volumetric and areal capacitance of electrodes did not differ. The volumetric capacitance at scan rate 1 to 100 mV s^{-1} lies in the limit $27\text{-}18 \text{ F cm}^{-3}$, the areal capacitance at scan rate 1 to 100 mV s^{-1} $0,39$ to $0,27 \text{ F cm}^{-2}$.



a) 300 times magnification, b) 10000 times magnification

Figure 2 – SEM images of AC-FWCNT electrodes

Table1 – Structure and capacitance values of the representative electrodes of this work

	~25 WS-FWCNT	25~53 WS-FWCNT	53~75 WS-FWCNT	WS-FWCNT
Thickness (μm)	136	154	139	148
Mass density (g cm^{-3})	0,195	0,185	0,200	0,191
Specific surface area (m^2/g)	1432	1436	1353	1145
Specific capacitance (F g_-1) (at 1–100 mV s^{-1})	135-101	136-99	133-100	138-96
Volumetric capacitance (F cm^{-3}) (at 1–100 mV s^{-1})	26-20	25-18	27-20	26-18
Areal capacitance (F cm^{-2}) (at 1–100 mV s^{-1})	0,36-0,27	0,38-0,28	0,37-0,28	0,39-0,27

Conclusion

It was 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. 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.

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