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Blend of low cost electrode material for energy storage device under DC glow discharge plasma exposed ESAC

ABSTRACT

The waste biomass in the form of eucalyptus globulus seeds activated carbon, which is employed as the electrode material and is environmentally acceptable, provides the good specific capacitance in the current work which is used for the energy storage application. A sample carbonization and physical activation procedure was used to create the activated carbon from the eucalyptus seeds. As prepared activated carbon was exposed to a DC glow discharge plasma, which modifies the surface of the material without altering its core characteristics. The investigation of the activated carbon was done utilizing structural, morphological, and electrochemical techniques of both pure and plasma treated. The increasing intensity of the X-ray diffraction indicates the carbon's amorphous and disorderly character. More oxygen-containing functional groups are present, according to an FTIR analysis. The FESEM/EDAX investigation has demonstrated the less appearance and more graphitic porosity with random orientation. Moreover, the electrochemical investigations were examined for utilization of the material of Electrochemical Impedance Spectroscopy (EIS) and Galvanostatic charge-discharge (GCD) which has a specific capacitance of 150F/g for a 1.5mA/g current density. The results revealed that the activated carbon made from Eucalyptus seeds after plasma treatment has good surface characteristics, improved specific capacitance, and is a low-cost electrode material for fabrication of energy storage device.

Keywords: Eucalyptus seeds, Activated carbon, Plasma treatment, Surface modification, Specific capacitance

1. INTRODUCTION

Now a day's energy storage device has been recent trends in the modern world where the world is depending on the energy sources. The focus of energy research has turned to advancing the development of sustainable and renewable energy sources due to the ever-increasing global energy demand, the decreasing availability of fossil fuels, and increasing environmental issues[1]. To full fill the next generation requirements its need, a major improvement in the energy density and cyclic life of present energy storage device. Batteries have exploring innovative energy material and associated high energy density storage for longer time period in order towards archiving its goal in the

energy storage system[2]. Recently, bio-mass, which is primarily agricultural waste, has become a different source of porous carbon and has been used in energy storage technologies. Here activated carbon derived from the Eucalyptus seeds serves as the good carbon material for the energy storage application. This Eucalyptus seeds activated carbon (ESAC) was undergoes the pyrolysis carbonization with the physical activation[3]. The ESAC was investigated using the structural and morphological characteristics, which observes that the carbon has the more porous morphology, whereas the electrochemical investigation shows the energy density of the material. The as prepared electrode of ESAC undergoes the electrochemical studies such as EIS and GCD to check the electrical conductivity of the material and the specific capacitance and cyclic stability and power density of the ESAC electrode material. On this results, we make an effort to present a summary of the most recent developments in the use of carbons obtained from

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the ESAC biomass as electrodes for new rechargeable batteries[4].

1.1. Plasma Introduction

The fourth state of matter is called a plasma, which is made up of extremely excited atoms, molecules, ions, and free radical species. Recently, plasma processing has taken over as the main source for altering a material's surface without affecting its fundamental qualities or bulk characteristics[5]. Plasma modification is used to create certain functional groups that can interact with other groups, change the surface's free energy, increase its ability to resist corrosion, alter its porous morphology, remove contaminants, or create cross-linking. The plasma surface modification could lead to the development of interaction of the carbon material with the increase and formation of new covalent bonds in the functional groups[6]. Along with this the adhesion strength, wettability and biocompatibility are also enhanced. When carbon materials are subjected to plasma treatment, the most significant features that can alter are an increase in surface area compared to untreated carbon materials. Normally, carbon is hydrophobic however, after plasma treatment, ESAC's wettability transforms to hydrophilic[7]. The as prepared carbon electrode material has the increased wettability of hydrophilic nature which have the redox behavior and the transfer of electrons. Thus the specific capacitance of carbon material can be improved by adding some more oxygen containing molecules in to the carbon

framework. It has been shown that after air plasma treatment addition of oxygen containing groups to carbon based material can increase the capacitance, improve surface wettability and to some extent boost electrical conductivity[8].

2. MATERIALS AND METHODS

2.1. Materials

The eucalyptus seed was viewed as the activated carbon's primary raw source. This raw materials were gathered in the Niligris area which serves as the basic resource. Before beginning the carbonization process, the raw material was cleaned several times with distilled water, dried in the sun, and then roughly crushed with a mortar and pestle to break up the globulus (spherical) shape for an easier carbonization process.

2.2. Carbonization

The pyrolysis method was used to carbonize the dried eucalyptus seed for an hour in a muffle furnace at a temperature of about 400°C at the heating temperature of 5°C/min. The hard carbonized particles were crushed into nanoparticle size using a mortar and pestle.

2.3. Activation

Followed by the carbonization process the nanoparticles sized carbon material undergoes the physical activation process in the same muffle furnace for about 600°C for an hour at the heating temperature of about 5°C/minute [9] shown in fig.1

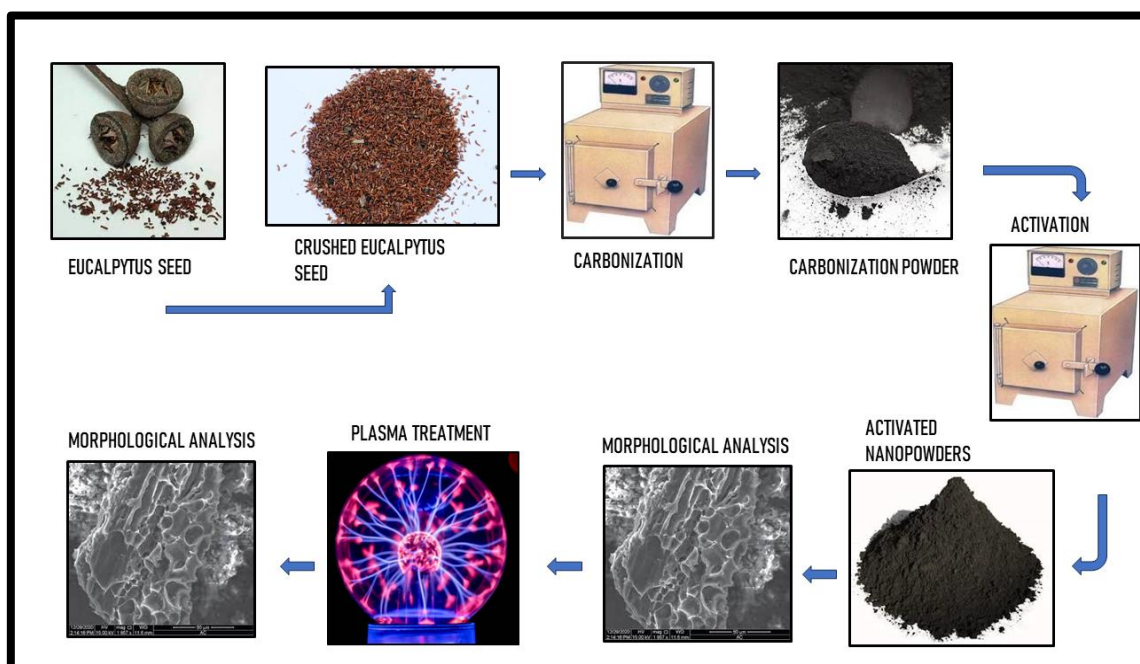


Figure 1. Schematic diagram of synthesized ES nanoparticles

Slika 1. Sematski dijagram sintetizovanih ES nanočestica

2.4. Plasma processing

The plasma chamber consist of two aluminum electrodes, a Pirani gauge power source, and stainless steel chamber 50*30-diameter gas valve which are all included. Using acetone and distilled water, the entire chamber was cleaned. The activated ES was collected in a sample holder that was sandwiched between two electrodes that were spaced 6 cm apart. The operatory parameters of DC glow discharge plasma is of about 450 V and 0.03 mbar pressure were used to create the atmospheric air plasma.

2.5. Electrode preparation

In order to get the active electrode material of ESAC, air plasma treated ESAC were developed by mixing as-prepared nanoparticles carbon black, and poly vinylidene difluoride (PVDF) were mixed in a mass ratio of 80:10:10 with 0.3 mL of N-methyl 2-pyrrolidone (NMP) to obtain the homogeneous slurry mixture. In a hot air oven, the active electrode was dried for three hours at 60 °C. Ag/AgCl and platinum act as the reference electrode and counter electrode. In a three-electrode configuration. The untreated ESAC and the plasma treated ESAC was used as the working electrode.

2.6. Characterization

The formation of the crystalline structure was investigated using XRD (XPERT-PRO with CuK

radiation).By using the Shimadzu 8400S FT-IR Spectroscopy instruments functional groups was analyzed. The crystal surface morphology was examined using a JEOL version JSM 6390LV, and the components and component ratios were verified using a JEOL version JED-2300 for EDAX technique. Three electrode systems were utilized to test the electrochemical properties with the PG LITE 1.0 electrochemical apparatus.

3. RESULT AND DISCUSSION

3.1. XRD (X-ray diffraction)

Fig. 2(A) displays the XRD patterns of the ESAC, These broad peaks for the activated carbon are located at around 23°, which corroborate the amorphous properties and disordered nature of the carbon due to (002) with the plane that indicates the graphitic nature[10]. Following the plasma treatment, the ESAC's intensity was proceed to increase without changing its basic properties[11]. By applying the Debye-Scherrer (Eq. 1), which determine the crystalline size between 30 to 40nm.

$$D = K\lambda/\beta \cos \theta \quad (1)$$

Along with this, the ESAC material's micro strain lies between 0.0081 to 0.01 and dislocation density ranges from 0.000170 to 0.020 was observed.

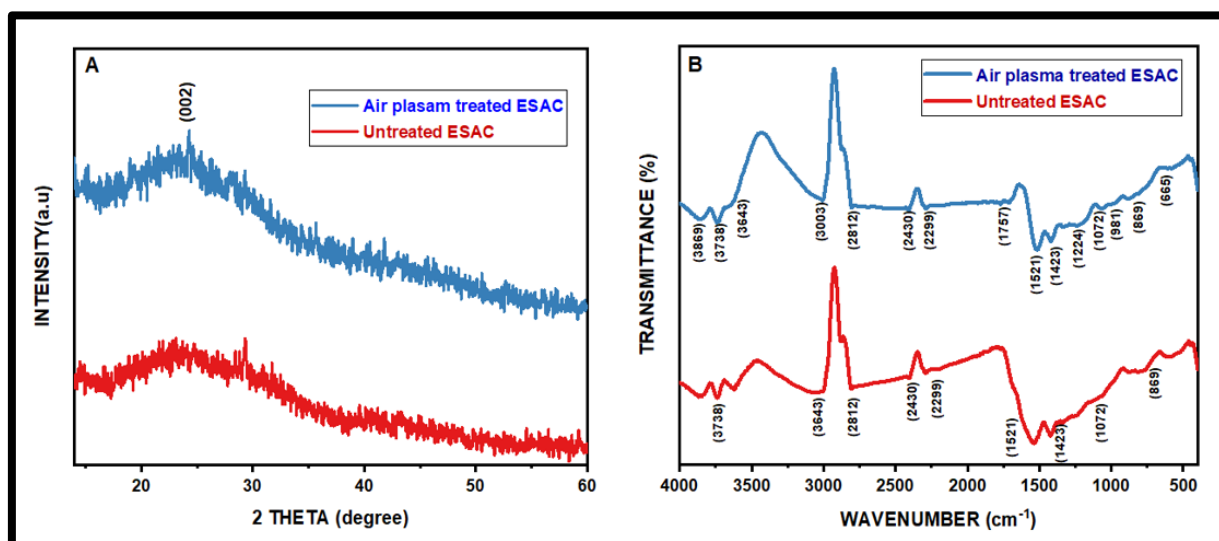


Figure 2. (a) The XRD diffraction peaks and (b) The FTIR spectra of untreated and plasma treated ESAC

Slika 2. (a) XRD difrakcioni pikovi i (b) FTIR spektri netretiranog i ESAC tretiranog plazmom

3.2. FTIR (Fourier Transform infrared spectroscopy)

The FTIR spectra of untreated ESAC was investigated which is ranging from 4000cm⁻¹to

400cm⁻¹ shown in fig 2(B). The peak at 3738 cm⁻¹-3643cm⁻¹ in the spectra is due to the stretching vibrations of the carboxylic group's O-H bond. The vibration band at 2812cm⁻¹ corresponds to the

methyl and methylene groups. The vibration peaks corresponds from 2430cm^{-1} to 2299cm^{-1} are assigned to the stretching of C-H mode[12]. The peaks ranging from 1521cm^{-1} to 1072cm^{-1} observed as stretching vibration of C=O as the carboxyl and carbonyl groups along with the aromatic ring, at 869cm^{-1} as C-H stretching. But after the air plasma treatment the increase in wettability has more polar region with covalent bonds. Thus shows the 3869cm^{-1} of O-H stretching of bonds and 3003cm^{-1} to 2812cm^{-1} has the carboxylic acid, phenols and alcohol groups. The peak at 1757cm^{-1} has the C=C aromatic ring. The vibration peaks ranging from 981cm^{-1} to 665cm^{-1} has the weak band of aromatic rings of C-H groups [13]. The material's surface area helps by supplying more active sites for adsorption peaks in the ESAC material.

3.3. FESEM (Field Emission Scanning Electron Microscope)

As shown in (Fig. 3).with the FESEM image of pure ESAC and the plasma treated, the ESAC is

created as a byproduct of the conversion of cellulose, hemicellulose, and lignin by the process of structural disordering of the remaining carbon. (Fig 3a) shows the no pores for the untreated ESAC whereas for the Air plasma treated ESAC the (Fig. 3b, 3c) shows the more porous and open porous as a result of the interaction of the free radicals with the ESAC, which has good morphology. The porous construction may offer a large number of pores, which would help to improve electrolyte ion transfer and thus increase the surface area. The quantity and type of oxygen-containing surface groups which remains almost constant throughout the activation process, but after the plasma treatment, the number of oxygen-containing groups increases. Additionally, the EDAX investigations reveals that elemental makeup of untreated and air plasma treated ESAC, which adds to the carbon and oxygen content of different levels and peaks. In this results, there is 82% of carbon and 18% of oxygen present in the air plasma treated sample (Fig. 3d, 3e).

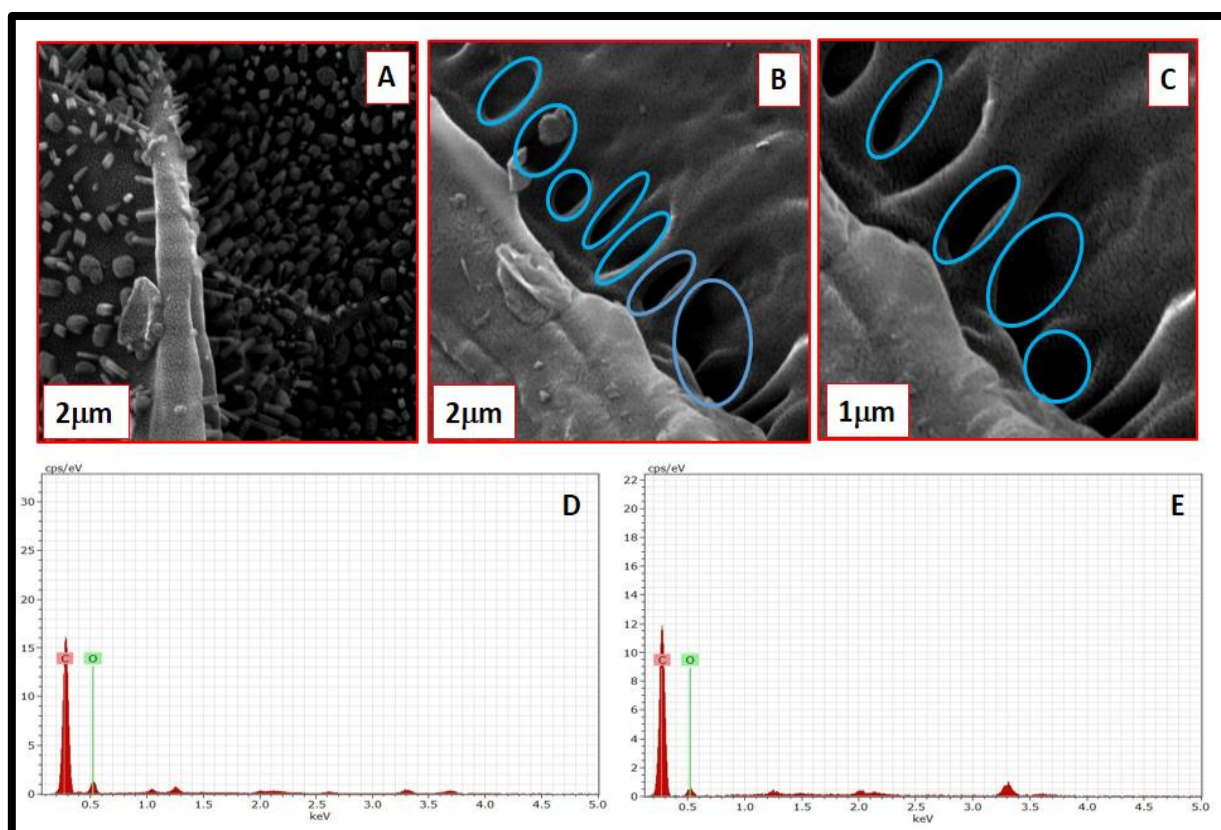


Figure 3. The FESEM /EDAX images (a) The untreated ESAC, (b) The air plasma treated ESAC, (c) The EDAX for untreated and (d) the air plasma treated ESAC

Slika 3. FESEM/EDAX slike (a) Netretirani ESAC, (b) ESAC tretiran vazdušnom plazmom, (c) EDAX za neobrađeni i (d) ESAC tretiran vazdušnom plazmom

ELECTROCHEMICAL INVESTIGATION

3.4. EIS (Electrostatic Impedance Spectroscopy)

In general, real- Z' and imaginary- Z'' value were carried out by electrochemical impedance analysis (EIS) for the Nyquist plot. The electrodes of both untreated and plasma-treated ESAC were examined using a 0.1MHz to 100 KHz frequency window, illustrated in (Fig.4). To describe Polarization Resistance (R_s) and Charge Transfer

Resistance (R_{ct}), the Nyquist plot indicates that the untreated ESAC in the frequency range is not a well-defined semicircle. However, after plasma treatment, the appropriate semicircle is a result of the charge transfer resistance, which suggests good charge conductivity. The equivalent polarisation resistance and the charge transfer resistance are calculated from the graph as for R_s 269 Ω and 1041 Ω for untreated ESAC and R_{ct} 103 Ω and 227 Ω for air plasma treated ESAC [14]-[15].

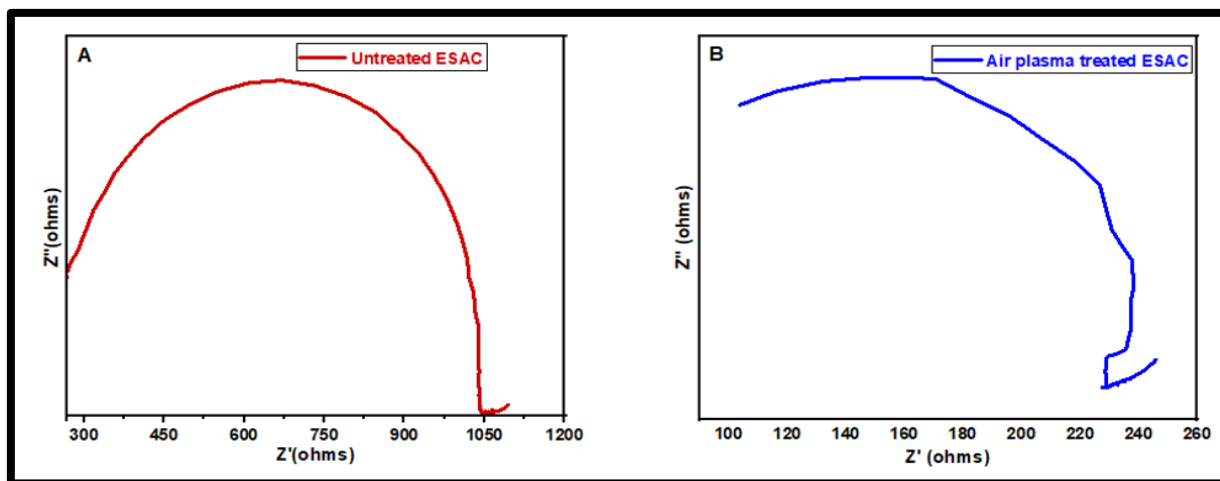


Figure 4. The EIS result (a) untreated electrode material ESAC and (b) The Air plasma treated ESAC electrode material

Slika 4. Rezultat EIS (a) neobrađen elektrođni materijal ESAC i (b) ESAC elektrođni materijal tretiran vazdušnom plazmom

3.5. GCD (Galvanostatic charge-discharge)

To further understand the electrochemical behavior the galvanostatic charge and discharge has been investigated using a three electrode system in 2M of KOH with potentials ranging from 0

to 0.5V and different current densities. The specific capacitance was investigated using the formula

$$C = \frac{I \cdot \Delta t}{M \cdot \Delta V} \quad (2)$$

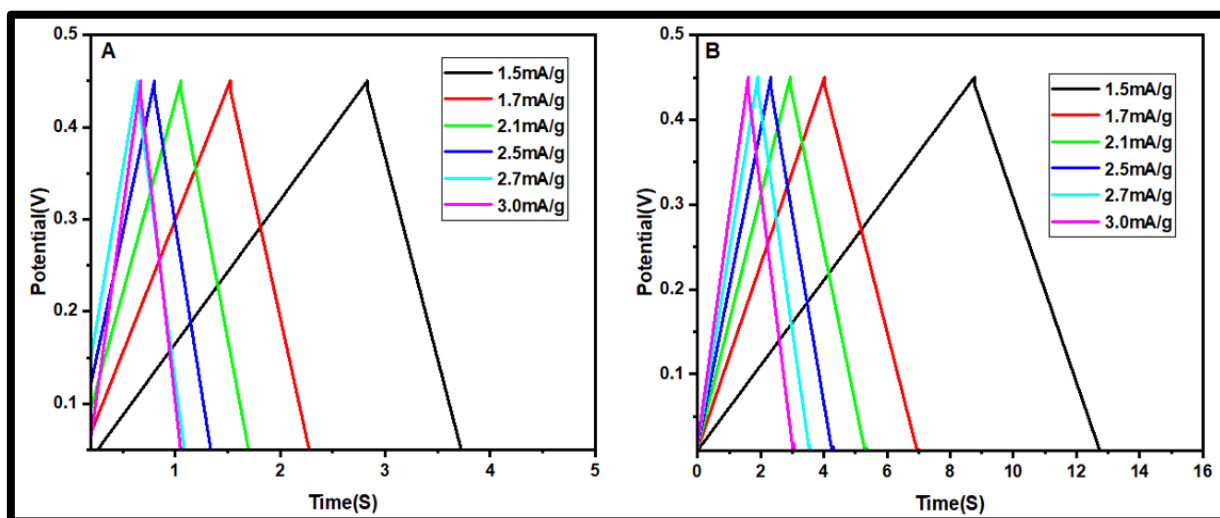


Figure 5. The GCD profile. (a) The untreated of ESAC and (b) The Air plasma treated ESAC electrode

Slika 5. Profil GCD. (a) Netretirana ESAC elektroda i (b) ESAC elektroda tretirana vazdušnom plazmom

The GCD profile in the figure 5 shows the current densities ranging from 1.5mA/g, 1.7mA/g, 2.1mA/g, 2.5mA/g, 2.7mA/g, 3.0mA/g. The specific capacitance has been calculated for both the electrodes of untreated and plasma treated ESAC, the untreated electrode shows the specific capacitance value of about 208F/g, 140F/g, 97F/g, 80F/g, 71F/g, 64F/g and [16], the plasma treated electrode shows the specific capacitance of about 613F/g, 444F/g, 375F/g, 350F/g, 323F/g thus the plasma treated ESAC electrode material due to its enhanced functional groups and the greater porous in the surface which render the material to hydrophilic nature and the plasma treatment thus increases the specific capacitance.

4. CONCLUSION

It was possible to create an activated carbon using the method of carbonizing and activating ESAC. The structural and morphological characteristics were investigated for both untreated and air plasma treated ESAC. The plasma treatment results in the formation of new functional groups that enhance the wettability, adhesion, and biocompatibility. The electrochemical results in the specific capacitance of 613F/g with the current density of 1.5 mA/g for KOH electrolyte. Thus it clearly shows how the plasma-treated carbon material improves in all of the aforementioned investigations and exhibits good electrochemical performance as well as environmental friendliness and economic viability.

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IZVOD

MEŠAVINA JEFTINOG ELEKTRODNOG MATERIJALA ZA UREĐAJ ZA SKLADIŠTENJE ENERGIJE ISPOD ESAC-A IZLOŽENOG DC SJAJNOM PRAŽNENJU PLAZMI

Otpadna biomasa u vidu aktivnog uglja semena eukaliptusa *globulosa*, koji se koristi kao materijal elektrode i ekološki prihvatljiv, obezbeđuje dobar specifični kapacitet u trenutnom radu koji se koristi za primenu za skladištenje energije. Korištena je procedura karbonizacije uzorka i fizičke aktivacije za stvaranje aktivnog uglja iz semena eukaliptusa. Kao pripremljen, aktivni ugalj je bio izložen DC usijanoj plazmi, koja modifikuje površinu materijala bez promene njegovih osnovnih karakteristika. Ispitivanje aktivnog uglja je obavljeno korišćenjem strukturnih, morfoloških i elektrohemijskih tehnika, kako čistih tako i tretiranih plazmom. Povećani intenzitet difrakcije rendgenskih zraka ukazuje na amorfnu i neuređeni karakter ugljenika. Prisutno je više funkcionalnih grupa koje sadrže kiseonik, prema FTIR analizi. FESEM/EDAKS istraživanje je pokazalo manji izgled i veću grafitnu poroznost sa nasumičnom orijentacijom. Štaviše, elektrohemijska ispitivanja su ispitana za korišćenje materijala elektrohemijske impedansne spektroskopije (EIS) i galvanostatskog pražnjenja-pražnjenja (GCD) koji ima specifičnu kapacitivnost od 150F/g za gustinu struje od 1,5mA/g. Rezultati su otkrili da aktivni ugalj napravljen od semena eukaliptusa nakon tretmana plazmom ima dobre površinske karakteristike, poboljšanu specifičnu kapacitivnost i da je jeftin elektrodni materijal za izradu uređaja za skladištenje energije.

Ključne reči: seme eukaliptusa, aktivni ugalj, tretman plazmom, modifikacija površine, specifična kapacitivnost.

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