Fabrication of Flexible Energy Storage Dielectric Material from Bio-Wastage

Monalisa Halder[1], Swarnava Halder[2], Anshit Mukherjee[3], and Ajit Kumar Meikap[4]

Abstract**-- Fossil fuels are a leading source of global warming pollution. Even the waste products are hazardous to public health and the environment. Considering the business cost and environmental concerns, the technology of 'Bio-waste-to-Energy' is recognized as an increasingly important renewable source of energy. Here we have produced potassium hydroxide (KOH) activated microporous carbon from tea wastage. We have fabricated flexible Polyvinyl alcohol (PVA: easily processable, cheap and eco-friendly polymer) based films using Activated Carbon (AC) as nanofiller with different weight percentage. Conductivity observation of the sample was done to study their prospect as the dielectric materials in energy storage, microwave absorption applications. Depending upon the results, we can apply the Activated Carbon (AC) based polyvinyl alcohol (PVA) dielectric film to make flexible, environmental friendly energy/storage devices, microwave absorbents.**

Index Terms**-- Activated Carbon; Biowaste Material; Dielectric Characterisation; Energy Storage; Polymer Film; Tea Wastage.**

I. Introduction

CARBON is an interesting material for more than a century. The allotropy of carbon makes it useful and applicable in different field of science and technology. In the very past, nanostructured carbon materials such as microposous AC, carbon nanotube (CNT) and graphene have been applied in various fields due to their distinct properties including mechanical, optical, electrical and electrochemical characteristics [1]. Nowadays, considering the business cost and sustainability of environment, the use of biowaste materials to produce higher value cactivated carbons (ACs) becomes one of the growing fields. Until now, various biomass materials, such as dates' stones, coconut shells, wood, rice husk, and banana peel were used as the precursor materials to produce ACs. The as-obtained microporous ACs have been used effectively in super-capacitors, catalyst carriers, solar energy conversion, electrode materials and adsorbents [2]. In India, a large amount of tea-wastage is produced in daily basis. India is the second largest producer of tea (famous Assam tea and Darjeeling tea) in the world after China. According to the Assocham report released in December, 2011, India, as the world's largest consumer of tea uses nearly 30 percent of the global output [3].

The tea-wastages usually are usually disposed by burning or by deposition in landfills that cause environmental harms. In this situation, conversion of tea-wastage to environment-friendly higher value products such as porous carbon/ activated carbon would be more preferable.

The magnificent properties of AC makes it suitable candidate for high-performance polymer composites. In order to increase the application range of polymers, nanofillers can be incorporated into the polymer matrix. The fabrication of flexible polymer based dielectrics with AC as filler element is very much desirable in the applications related to microwave absorbing property such as antenna techniques, protection of humans and other biological objects from the harmful effect of the electromagnetic waves, military application [4].

Here we have produced potassium hydroxide (KOH) activated porous carbon from tea wastage and studied its physical characterization with XRD, UV-Visible spectra. Also we studied the elctrochemical properties of the activated carbon. The cyclic voltammetry, galvanostatic charge discharge and electron impedance spectroscopy measurement was done. We have fabricated flexible Polyvinyl alcohol (PVA) based nanocomposite films using AC as nanofiller with different weight percentage. Electrical characterisation of the films was done to study their prospect as the materials in energy storage, microwave absorption applications.

The work was financially aided in part by DST-SERB (Grant No. EMR/2016/001409), Govt. of India.

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FOSET special issue on Recent innovations in Engineering, Science and Technology
Volume 1, Issue 1
https://doi.org/10.15864/ajac.21003

II. Experimental Section

A. Synthesis of Activated Carbon

At first the tea wastage was collected from household. The pre-treated tea wastage was mixed with potassium hydroxide (KOH) at a ratio 1:1. The mixture was placed in porcelain boat and put in a furnace under constant Argon and heated at a temperature 1023 K. The whole process was done under Argon atmosphere. The sample was washed several times with deionized water and filtered. Then the sample was heated at a temperature 338 K. By crushing it in smooth powder, the activated carbon was achieved.

Fig. 1. Flowchart of digital images of synthesis of KOH activated carbon

B. Synthesis of Flexible Polyvinyl Alcohol (PVA) Nanocomposite Films Using Synthesised Activated Carbon (AC) Nanofillers

The flexible PVA nanocomposite films with AC as nanofillers were processed by the solution casting method. The solutions (PVA with inclusion of 2 wt % AC, 4 wt % AC)were poured into glass petridice and dried in natural environment for 6 days. Pure PVA is marked as R_1. R_2 is 2 wt % AC-PVA and R_3 – 4 wt% AC-PVA.

Fig. 2. PVA solution under continuous stirring at the rate of 430 rpm

C. Characterisation Methods

UV-Vis absorption spectroscopy of TW and AC has been done in the wavelength range from 200-800 nm, using UV-Visible spectrophotometer (HITACHI-3010). Electrochemical measurement of synthesised activated carbon (AC) is conducted in a three electrode cell using an electrochemical workstation by several procedures such as cyclic voltammetry (CV), galvanostatic charge discharge (GCD) and electrochemical impedance spectroscopy (EIS). The 3-electrode electrochemical cell is made up of a working electrode, Ag/AgCl reference electrode and platinum counter electrode. With the help of LCR meter, electrical properties of the prepared film samples are measured.

III. Characterization, Results & Discussions

A. UV- Visible Analysis

The optical absorption spectra of the tea wastage and activated carbon were measured using a UV spectrophotometer. Ethanol was used as the solvent for the measurement. Figure 3 shows the absorption peaks for raw tea wastage and KOH activated carbon. For the raw tea wastage, we see one major absorption peak from 250 nm to 290 nm, with the peak at 273 nm. This absorption peak is assigned to functional groups attached to aromatic ring, which includes –OH (270 nm). There is also another peak around 410 nm which is the characterization peak of β carotene which is an antioxidant that converts to vitamin A. There is another small peak around 664 nm which is due the presence of chlorophyll [6-11]. For the UV spectra of activated carbon, there is only one peak is visible which is at λ=270 nm. This peak corresponds to aromatic compound presence in the activated carbon. Peak around 270 nm also represents the π-π* transition in aromatic compound.

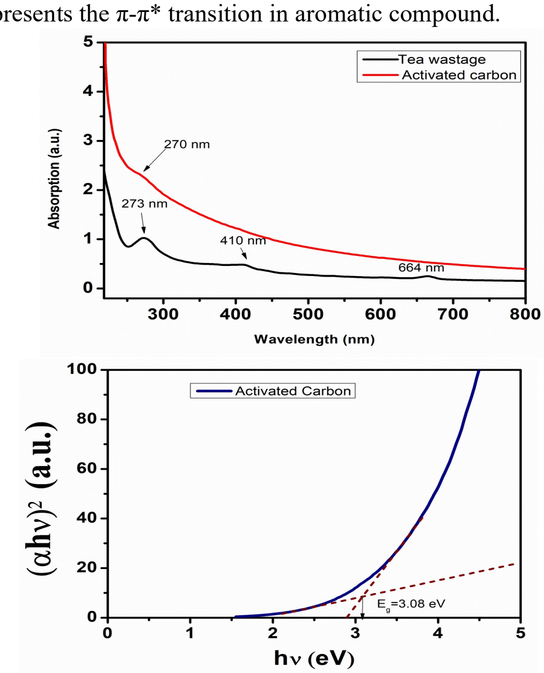

Fig. 3 (a) UV-VIS spectroscopy of tea wastage and activated carbon, (b) Tauc plot (Direct transition) of Activated Carbon

From the Tauc Plot [Fig. 3 (b)], it is obtained that E_{nano}= 3.08 eV. Determination of band gap demonstrate that activated carbon behaves as semiconductor material and therefore also as a photoactive material in the presence of UV light as the E_g < 4 eV [12]. So activated carbon can be used as a as a photoactive material in application in optoelectronics.

B. Electrical Measurement (Cyclic Voltammetry)

The most valuable property of a supercapacitor is its ability to supply energy density & electrochemical analysis. To find the electrochemical performances of activated carbon, the cyclic voltammetry measurement was done which is a type of potentiodynamic electrochemical measurement. The measurement was done at room temperature between the potential range of 0 to 1 V. Figure 4 shows the CV curves of activated carbon at various scan rates. The shape of the curves upto the scan rate 100 mV/sec are rectangular which represents a good capacitor like characteristics and also electric double layer capacitance [7]. But the rectangular curve gets deformed after the scan rate 200 mV/sec. It is also noticed that as the scan rate increases, the current density also increases. It is also found that there are no peaks in CV curve which means the supercapacitive property is free from redox reactions.

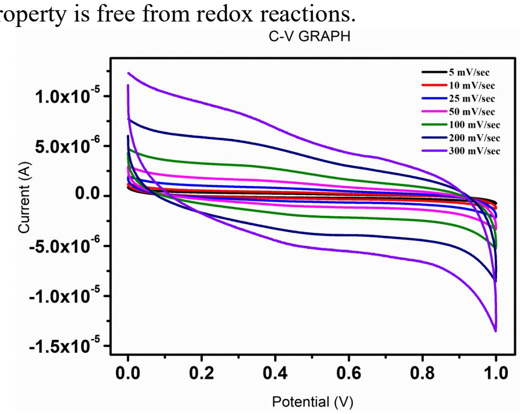

Fig. 4. Cyclic Voltammetry curves of KOH activated carbon

C. Electrical Measurement (Galvanostatic Charge Discharge)

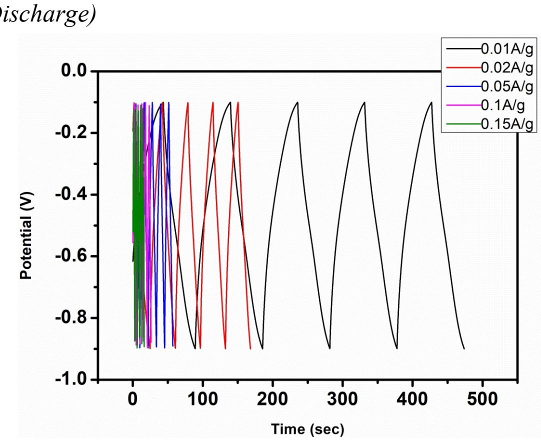

Fig. 5. GCD curve of Activated Carbon for different current densities

Figure 5 shows the Galvanostatic Charge Discharge (GCD) curves for activated carbon recorded for different current densities. As seen from the figure, for all current densities, the curves show similar symmetrical triangular curves. As the current density increases, the charge discharge time becomes lesser. As seen from the curves, a drop in discharge arises due to the diffusion-limited mobility of the electrolyte ions [6]. The GCD curves show that the KOH activated carbon is behaving like a typical carbon based supercapacitors.

D. Electrical Measurement (Electrochemical Impedance Spectroscopy)

Figure 6 shows the EIS data expressed as Nquist plots in frequency range 100 Hz – 106 Hz for KOH activated carbon. In high frequency region, small semicircle represents resistive nature of supercapacitive system.

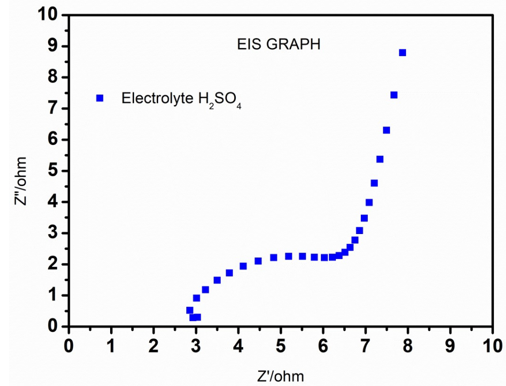

Fig. 6. EIS curve of Activated carbon using 1M H_2SO_4 as electrolyte

E. Conductivity Study

Frequency variation of total conductivity is being investigated in the range of 20 Hz – 2 MHz above room temperature for the nanocomposite film samples (R_2, R_3). When frequency is low, then the conductivity remains unchanged with the variation in frequency. This phenomenon suggests the dominance of DC contribution. But the frequency dependence of conductivity is noticeable in the higher frequency range. Using Arrhenius equation, activation energies of the film samples are calculated and indexed in Table 1. According to Jonscher, the conductivity relation can be written as follows, [14]

$$\sigma(f) = \sigma_{dc} + \sigma_{ac}(f) = \sigma_{dc} + A f^{S} \quad (1)$$

The frequency exponent S have been extractedfrom $\ln \sigma(f, T)$ vs. $\ln f$ plot. From figures, S decreases when we increase the temperature. Here, the nature of S shows Correlated Barrier Hopping (CBH) model type conduction where, mobile charges hop over a potential barrier between two defect sites. The modified equation of frequency exponent S is given as [14],

$$S = 1 - \left(\frac{6 k_B T}{W_m} \right) \quad (2)$$

where k_B, Wm are Boltzmann's constant and maximum barrier height respectively. From the result it can be concluded that the maximum barrier height is least in AC-

FOSET special issue on Recent innovations in Engineering, Science and Technology
Volume 1, Issue 1
https://doi.org/10.15864/ajac.21003

PVA (2 wt %) nanofillers loaded PVA nanocomposite film (Table 1).

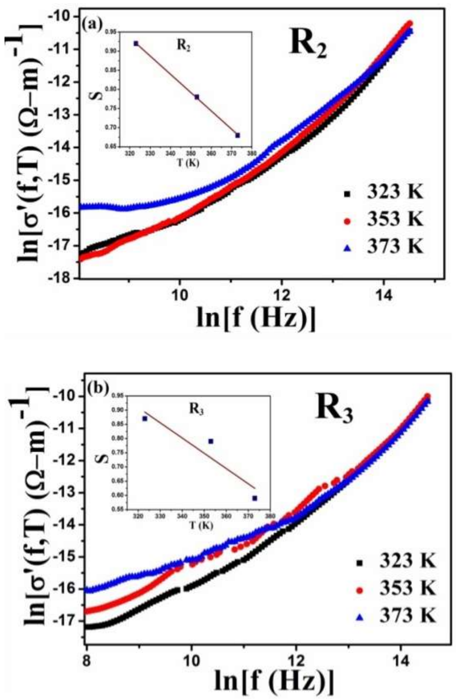

Fig. 7. EIS curve of Activated carbon using 1M H_2SO_4 as electrolyte.

TABLE I

Samples of Times Roman Type Sizes and Styles

Samples	Maximum Barrier Height (W_m)	Activation Energy (E_A)
R_2	**35 meV**	**0.88 eV**
R_3	**31 meV**	**0.28 eV**

IV. CONCLUSION

In conclusion, we successfully converted tea wastage collected from household and prepared activated carbon (AC) by potassium hydroxide (KOH) activation process. Then the physical characterizations of the prepared AC were done using UV spectroscopy. Also the electrochemical property of the activated carbon was studied and the results were similar to a carbon based supercapacitor, which was expected. Also the electrical transport properties were studied. Depending upon the results, we can apply the Activated Carbon (AC) and AC-PVA film to make flexible, environmental friendly storage devices, microwave absorbents.

V. ACKNOWLEDGMENT

The work is financially aided by DST-SERB (Grant No. EMR/2016/001409), Govt. of India. Authors would like to acknowledge DST-INSPIRE, Govt. of India, for providing fellowship and scholarship.

VI. REFERENCES

[1] W.-K. Chen, *Linear Networks and Systems.* Belmont, CA: Wadsworth, 1993, pp. 123–135.

[2] T. Adinaveen, J. J. Vijaya, L. J. Kennedy. *Arab Journal of Science and Engineering* 41 (1), 2016, pp.55-65.

[3] C. Peng, X. B. Yan, R. T. Wang, J. W. Lang, Y. J. Ou, Q. J. Xue. *Electrochimica Acta* 87, 2013, 401

[4] https://en.wikipedia.org/wiki/Indian_tea_culture

[5] A. Sehemi, G. Abdullah, A. Ghamdi, A. Ahmed, Dishovsky, Nikolay, Nickolov, N. Radostin, Atanasov, T. Nikolay, L. T. Manoilova. *Materials Research* , 20 (5) 2017.

[6] A. B. Bogeat, M. A. Franco, C. G. Fernández, A. G. Macías, V. S. Gómez. *Physical Chemistry Chemical Physics,* 2014,16, pp. 25161-25175

[7] R. Farma, M. Deraman, Awitdrus, I. A. Talib, R. Omar, J. G. Manjunatha, M. M. Ishak, N. H. Basri, B. N. M. Dolah. *International Journal of Electrochemical Science* 8, 2013, 257

[8] M. Halder, A. K. Das, A. K. Meikap. Materials Research Bulletin 104, 2018, pp. 179-187

[9] S. Khppmprtezaei, M. R. Golobostanfard, H. Abdizadeh. Conference Paper (2017)

[10] V. Grillini, P. Verlicchi, G. Zanni. *Water.* 14(2) 2022, 243.

[11] A. Lim, K. U. Tennakoon, L. Lim, S. Bandara. *International Journal of Biophysics* 2015, 510467.

[12] A. Belay, K. Ture, M. Redi, A. Asfaw. *Food Chemistry* 108 (1), 2008, pp. 310-315.

[13] I. V. Gala, J. J. L. Peflalver, J. R. Utrilla. *International Journal of Chemistry* 7 (1), 2015.

[14] S. Nasir, M. Z. Hussein, Z. Zainal, N. A. Yusof, S. A. M. Zobir. *MDPI Energies* 11(12), 2018, 3410

[15] A. K. Jonscher. *Nature* 267, 1977 Nature pp. 673–679.

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