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RESEARCH ARTICLE

CAPACITIVE PERFORMANCE OF ONION PEEL DERIVED CARBON

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ABSTRACT

Carbonaceous material has been derived from a domestic biomass waste *viz*., onion peel and assessed its suitability as electrodes in electrochemical double layer capacitors (EDLC). Onion Peel Carbon (OPC) has been obtained from pyrolysing onion peel under N_2 atmosphere without any porogens or activating agents. Physical characterization of OPC by X-ray diffractometry, Infra Red spectroscopy, Scanning Electron Microscopy and elemental analysis followed by a critical assessment of its electrochemical behavior in H_2SO_4 electrolyte by cyclic voltammetry and galvanostatic charge-discharge cycling studies. Cyclic voltammetry estimates specific capacitance values as high as 206 F/g at a scan rate of 10 mV/sec. The specific capacitance decreases on increasing the scan rate. The results of the studies infer that OPC has immense application as electrochemical double layer capacitor electrode. The work thus contributes not only towards a waste utilization concept but also presents a new and valuable dimension to the usefulness of onion peel in energy storage systems like capacitors, hitherto unexplored.

INTRODUCTION

Electrochemical capacitors (or) supercapacitors (SCs) are becoming technologically important for low-power gadgets like PC cards, photographic flash, flashlights, portable media players and automated meter reading equipments, although their widespread usage has not been attained due to a high cost to performance ratio (Hall *et al.,* 2010). Exploding research is thus being conducted to lower the costs of the capacitors through the engineering of new materials. Needless to say that selection of appropriate electrode materials and electrolyte systems is fundamental in determining the device performance. Currently the most viable materials used as electrodes in electrochemical capacitors are metal oxides (Novak *et al*., 1997) and conductive polymers (Zhou *et al*., 2004), in addition to the other conventional carbon materials like activated carbons (ACs) (Wang *et al*., 2007), carbon aerogels (Fang *et al*., 2007), graphites (Mitra and Sampath 2004), carbon nanotubes (Honda *et al*., 2007) carbon nanofibers (Kim and Lee 2004), and nano sized carbons (Sivakkumar *et al*., 2007). However, the preparation processes for these carbons require expensive and non-renewable raw materials, a lot of time and energy and tedious preparation procedures. By contrast, plant biomass wastes are very cheap and omnipresent, serve as potential raw materials for the production of carbons with good electrochemical performance. Manufacture of activated carbon from bio-wastes is thus gaining significance as high valued scientific, industrial and engineering product could be effectively manufactured from almost zero-cost raw materials. Over and above the utilization of biomass wastes also provides a solution for waste disposal.

Survey of recent research reports shows that a number of carbon materials derived from plant biomass have been utilized as electrode materials for SCs (Jisha *et al*., 2009, Subramanian *et al*., 2007, Li *et al.,* 2010, Rufford *et al*., 2010). Nevertheless, the choice of carbon electrode materials has to be explored in order to achieve the ever best capacitance value. Hence, from this view point the feasibility of obtaining carbon from a common domestic waste viz., Onion Peel has been explored for applying as an electrode material for EDLCs in acid medium. Accumulation of onion peel has risen over recent years in line with the growing demand for these bulbs. More than 1,000,000 tons of peels are generated in the world each year and large quantities of the onion peel are left to rot on the fields and hence one facile solution could be to use this waste as a natural source of carbon by pyrolyzing the peel waste. Thus onion peel can be thought of as interesting source for cost effective carbonaceous materials that could be employed as electrode material for supercapacitors. To best of our knowledge utilization of onion peel for obtaining carbon for supercapacitor electrode application has never been undertaken. Nevertheless, it is interesting and valuable to note that (Avisha Chowdhury *et al.,* 2012) had made use of onion and garlic peel for adsorbing Cu^{2+} from aqueous solution.

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Thus in the present work we have explored the physical features of the onion peel derived carbon and have evaluated the capacitive nature in acid medium to establish the usefulness of the discarded waste.

Experimental

Preparation of Onion Peel Carbon (OPC)

Onion Peel was collected from the market and washed several times with hot de-ionized water after which they were pat dried with wet tissue paper and ~10g sample was crushed using a blender. The crushed peel was immediately pyrolized under flowing N_2 at 500^{o}C at a heating ramp of 5^{o} min^{-1} for a hold period of 1 hour, furnace cooled to give a mass of char. (Peled *et al*., 1998) have observed that larger sample size may lead to abundant pyrolysis products which may attack the newly formed carbon surface, causing an increase in the surface area and destruction of the carbon bulk. In order to avoid the bad effects on the electrochemistry of the carbon powder, the authors took an optimum size of 10g of the raw material. The char was finally washed with hot de-ionized water until the pH of the decant solution was approximately 7 and colorless (null absorbance in the visible region) and dried. The powder so obtained after drying and grinding is hereafter called OPC to refer the onion peel derived carbon.

Physico-chemical characterization of the carbon sample

X-ray diffraction patterns were recorded on X'Pert Pro X-ray diffractometer with CuK_{α} radiation source. The surface functional groups on the biomass carbon were ascertained using FT-IR spectrometer (Model # Nexus 670) in the range from 4000 cm^{-1} to 400 cm^{-1}. Elemental analysis of the OPC was done by Vario ELIII CHNS/O elemental analyzer. Hitachi S-4700, field emission scanning electron microscope was used to examine the morphology of the carbon.

Electrode preparation and electrochemical measurements

OPC, were mixed with poly vinylidene fluoride binder and carbon black respectively in the weight ratio 85:10:5 to get slurry using N-methyl 2 pyrrolidone. The paste was smeared on to the circular end of an SS rod of 1cm^{2} area & length 8cm and dried at 80 ^{0}C for 1hour. Heat shrinkable sleeve was used to mask rest of the electrode portion. A three-compartment cell was constructed using the SS rod coated with OPC, Pt wire and SCE as the working, counter and the reference electrode respectively. Electrochemical studies (Cyclic Voltammetric and galvanostatic charge-discharge) were performed with CH Instruments (Model # CHI660a) 1M H_2SO_4 was employed as the electrolyte for assessing the electrochemical features of the OPC. The specific capacitance was evaluated from the area of the charge and discharge curves of the CV plot. Galvanostatic charge/discharge experiments were performed in a similar setup as described above with a current density of 10 mA/g and between 0.0 and 1.0 V.

RESULTS AND DISCUSSION

XRD Analysis

Fig. 1 shows the XRD pattern of the biomass carbon. The broad reflection between 23^{o} and 30^{o} indicates (002) diffraction peak, which is attributed to the amorphous and low graphitization features of the OPC. The nature of the peak may also indicative of the evolution of microporous carbon and the microporous structure is amorphous with enormous degree of non-crystalline signatures (Alcantara *et al*., 2007). It is presumed that a large number of disordered single graphene layers and stacked structures of graphene sheets may be present simultaneously in the texture of the carbon powder (Zhang *et al*., 2007) and the slightly broad shape also indicates the highly disordered structure in the carbon (Dahn *et al*., 1993). It is to be noted that the interplanar space (d_{002}) calculated for the OPC is 3.78 Å, higher than that reported for graphite (3.354 Å) again indicating considerable disorderliness in the carbon produced (Kyotani *et al*., 1997). Generally the value of d_{002} is taken as a measure of estimating the degree of graphitization in the carbon and the growing disorder is now reflected in the observed larger values of d_{002} of the OPC. The reflection around 43^{o} has been attributed to the (1 0) bidimensional planes (Inagaki 2009). The presence of h k (1 0) lines evidences the turbostatic or convoluted stacking of hexagonal layers of carbon resulting in disordered structure and lower crystallinity (Viswanathan *et al*., 2009).

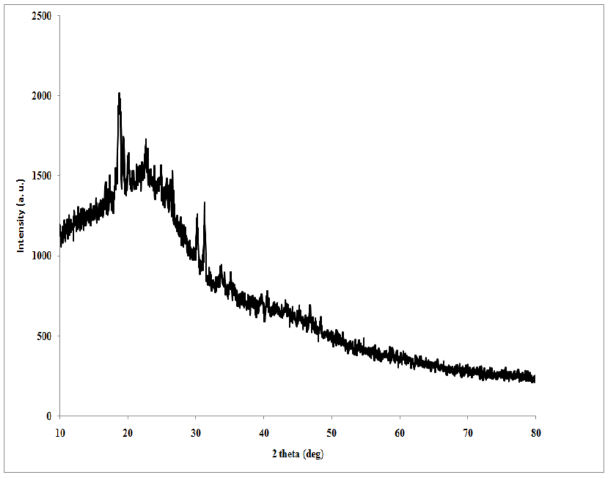

Fig. 1. X-ray diffractogram of OPC

Scanning electron microscopic (SEM) imaging and surface area measurements

Fig. 2 depicts the SEM of OPC at X1500 magnification. The micrograph shows sheet or bits of paper like morphology also offering crumbled or crushed appearance to the OPC. Further the particles lack porosity. It is now rather difficult to offer any correlation between the particle morphology and the electrochemical activity. Surface area of the OPC sample was measured as 642 m^{2}/g. A high value of the surface area may probably indicate the presence of enormous electrochemically accessible sites or area thereby resulting in increased electrochemical performance ultimately, which will be made obvious from the results of the electrochemical studies.

Functional group analysis or surface chemistry characterization studies

The electrochemical properties of any carbon depends on the physical properties as well as the nature and chemical reactivity of the functional groups present on the carbon surface. So gaining knowledge on surface functional groups would give us an insight to correlate the electrochemical properties of the carbon. As FT-IR spectroscopy is applicable for qualitative characterization of the surface functional groups, IR spectrum of OPC has been depicted in Fig. 3. The spectrum shows highly complex signatures, indicating the presence of many polar surface functional groups. These organic functionalities containing oxygen, imparts hydrophilicity to the carbon electrode and bring out strong interaction between the aqueous electrolyte ions and the polar groups in the carbon material and thus plays an important role for the performance of EDLC (Centeno and Stoeckli 2006)

As seen in the spectra, a strong wide absorption band at 3600-3300 cm^{-1} with a maximum at about 3387 cm^{-1}. The position of the band is characteristic of the stretching vibration of hydroxyl compounds while broadening of the band is indicative of high degree of association because of extensive hydrogen bonding. The bands at 2926 and 2856 cm^{-1}, which are assigned to asymmetric C-H and symmetric C-H bands, present in alkyl groups such as methyl and methylene groups. Stretching absorption band at 1629 cm^{-1} is assigned to in-plane O-H stretching of hydroxyl group. The characteristic peak at around 1365 cm^{-1} is owing to CH_2 group. The band at 1319 cm^{-1} have been assigned to C-O-C stretching of esters, ether groups and phenol derivatives. On the other hand,

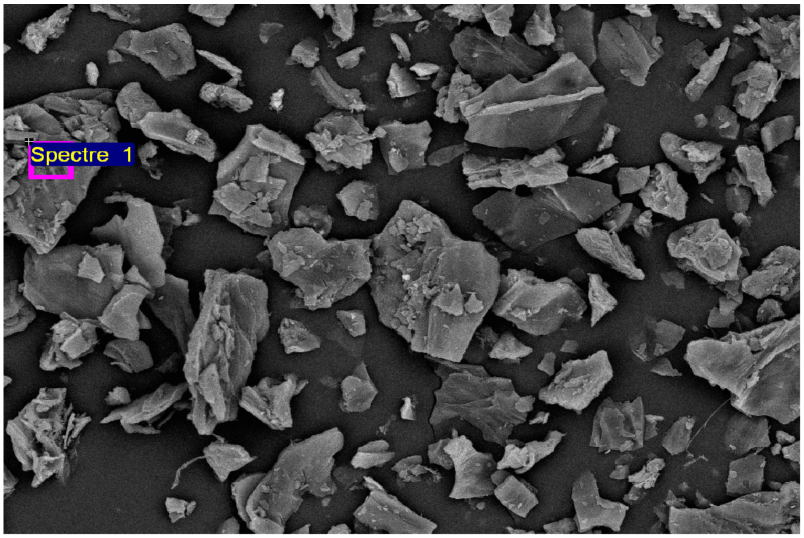

Fig. 2. SEM image of OPC

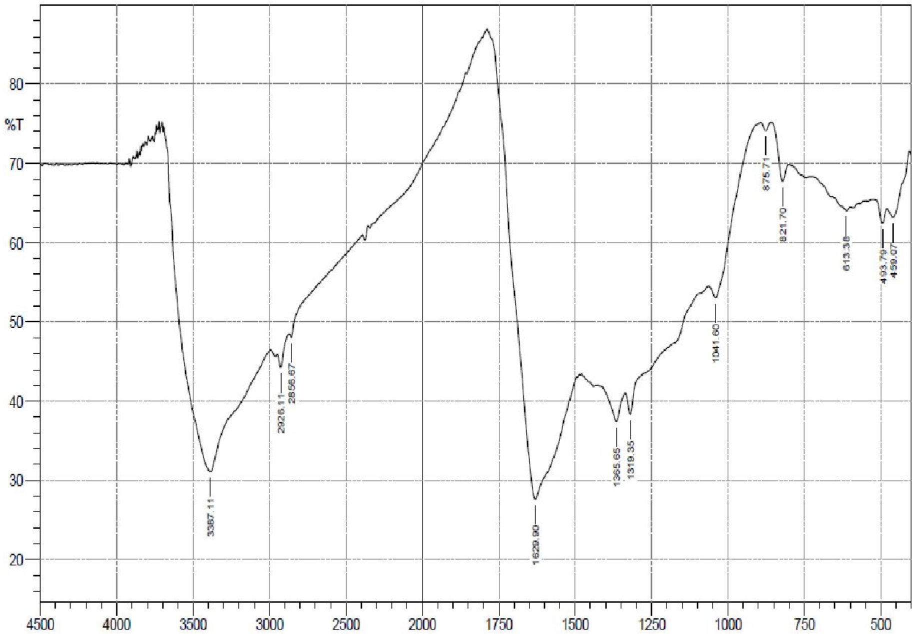

Fig. 3. FTIR Spectra of OPC

characteristic peak at 1041 cm^{-1} corresponds to C-O bond in alcohol. A characteristic peak observed at 807 cm^{-1} corresponding to out-of-plane C–H stretching vibration.

From this study it could be inferred that the surface of the OPC might contain carbonyl, alcohol, ester, ether and acetyl derivatives groups. The absence of N and S was ascertained by the ultimate analysis. Therefore, the prepared materials are mainly composed of amorphous carbons with different oxygen containing surface groups. These carbon-oxygen surface groups may exercise a profound effect on the surface properties of activated carbons and thus influence their electrochemical characteristics.

Ultimate Analysis

The biomass carbon consists of carbon atoms, which form aromatic sheets cross-linked in a random manner, and heteroatoms like oxygen, nitrogen, sulphur, hydrogen. The type and % of the constituents in biomass carbon depends on the nature and source of the raw material used and obviously on the thermal, physical or chemicals treatments (Kirubakaran *et al*., 2009). As the electrochemical parameters are influenced by the heteroatoms on the carbon matrix, ultimate elemental analysis on the OPC has been conducted. The heating rate controls the rate of volatile evolution from the biomass during pyrolysis and so slow heating and longer times gives high char yield (Katyal *et al*., 2003). Pyrolysis of onion peel yielded OPC which contains 59.2 wt% carbon with certain amount of H (4.1%), S (0.0%) and N (0.0%), but the total amount of these elements in weight is less than 100%. On the basis of previous reports about thermally-treated carbon material, the remaining component of the carbon material should be oxygen (Eshkenazi *et al*., 2004). FTIR data also supports the presence of oxygen containing organic functional groups, which may influence the electrochemical behavior of the carbon samples prepared.

Electrochemical characterization

Cyclic Voltammetric (CV) studies

CV studies explore the capacitive behavior of the OPC electrode in H_2SO_4 electrolyte. The effects of scan rate on CV is illustrated in Fig. 4. The specific capacitance values have been calculated using the equation, C = i/sm (F/g), where i, s and m are the average current, the scan rate and the mass of the active material (Senthil kumar *et al*., 2011).

CV depicted in Fig. 4 maintains distorted rectangular shapes for all the scan rates with discernible redox transitions at 0.8 and 0.1 V. It has been stressed in FTIR studies and from the results of other authors (Naoi *et al*., 2005) that the OPC like any other biomass derived carbons contains various organic moieties that would interact with the electrolyte ions leading to interesting electrochemical picture. In a typical acid, the following interactions with the phenyl (-Ph) and alkyl (-R) groups were reported by Hu *et al* 2007 as,

$O = Ph = O + 2H^+ + 2e^- \leftrightarrow HO - Ph - OH$;
$R = O + H^+ + e^- \leftrightarrow R - OH$

These reactions offer pseudo faradaic capacitance. So the total capacitance value of OPC has a contribution not only from the electric double layer charging but also from the pseudocapacitance of electroactive functional moieties. Dependence of specific capacitance of OPC electrode with scan rates is understood from Table 1. Specific capacitance value as high as 206 F/g has been obtained in 1M H_2SO_4 at 10 mV/sec scan rate, which may be attributed to the fact that the ions can diffuse into pores more easily (faster kinetic process) when the first cycle is completed (Lust *et al*., 2003). The electrochemical storage in activated carbon electrodes has been explained by the electrical double layer theory it suggests that ions occupy the pores in the carbon and participate in the formation of the electrochemical double layer. At higher scan

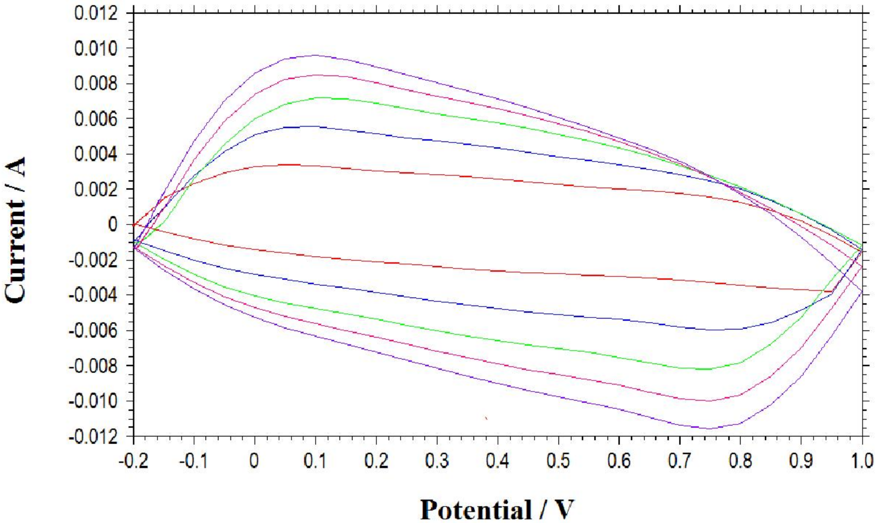

Fig. 4. CV of OPC electrode in 1M H_2SO_4 electrolyte

Table 1. Dependence of specific capacitance of OPC electrode with scan rate

Scan rate (mV/sec)	Sp. Capacitance (F/g)
10	206
20	165
30	146
40	143
50	133

rates as each cycle finishes quickly the ions cannot diffuse in to the pores as faster as the cycles. Poor performance of the electrode at higher scan rates has been ascribed to (Jisha *et al*., 2009). In this regard, OPC powder may be useful as an electrode material in capacitor applications.

Galvanostatic charge/discharge cycling studies

Galvanostatic charge–discharge cycling studies explore the performance of the electrode from OPC carbon. Fig. 5 shows the galvanostatic charge–discharge cycle profile (15 cycles) of OPC electrode recorded from 0 to 1 V at current density 10mA/g. Galvanostatic charge-discharge measurement shows the isosceles triangular shape with the discharge time close to that of charge, reflecting high charge–discharge efficiency of OPC electrodes.

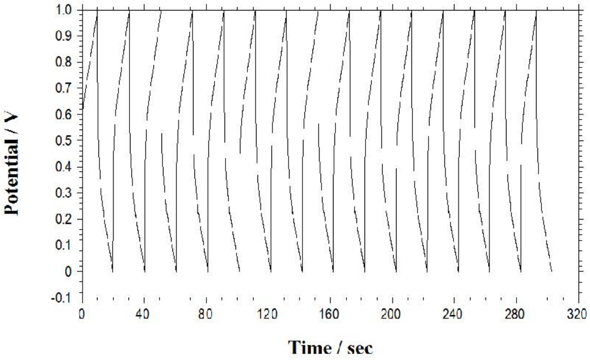

Fig. 5. Galvanostatic charge-discharge cycles of OPC

The symmetricity of the isosceles triangle was influenced by the difference of charge and discharge time. If the difference of charge and discharge time was less, then the isosceles triangle shape is more symmetric. The more symmetric the triangle, the higher will be the charge–discharge efficiency of EDLC (Yafei *et al*., 2008). The reversible redox reactions of surface functional groups generate pseudocapacitance during charge-discharge processes and so there is enhancement in the total capacitance (Yafei *et al*., 2008).

In general, the double-layer formation and the resulting capacitance has a strong dependence on the concentration of the electrolyte and the high surface area arising from the porous structure of the carbon. As explained from the results of CV studies, better ionic diffusion in to the pores of the carbon is observed, due to the presence of H^+ ions as the mobile species in H_2SO_4 electrolyte, resulting in an enhanced EDLC performance. Ultimately, the capacitive currents and hence the total capacitance values of OPC has contributions both from the double layer charging and the pseudocapacitance of electroactive functional moieties.

The gravimetric specific capacitance was calacuated using the following formula

$$C\ (F/g) = i\Delta t/m\Delta V$$

where i is the current used for charge – discharge; Δt is the time elapsed for the charge or discharge; m is the mass of the active electrode and ΔV is the voltage interval of the charge or discharge. The high charge–discharge efficiency of OPC based electrodes indicates that electroactive carbon particles contacted well with electrolyte solution, or in other words the electrodes had a high hydrophilicity of their surface. Thus the OPC in acid medium has high specific capacitance and high charge–discharge efficiency.

Conclusion

Vegetable sources are gaining significance as hi-end products like carbon and activated carbon could be effectively produced from these zero-cost raw materials. The fact has been established through our results reported here by way of utilizing a household waste biomass. Carbon powder has successfully been produced by pyrolyzing the biomass of onion peel and has been electrochemically characterized for the possible application as electrode material for supercapacitors. Performance of the biomass derived carbon has been evaluated in 1M H_2SO_4 aqueous electrolyte. The observed capacitance value of 206 F/g at 10mV/sec scan rate has been attributed to the combination of pseudocapacitance and double layer charging coupled with physical properties and the surface organic functionalities on the biomass carbon. Simple preparation process, the availability of the biomass in large scale and impressive capacitance value might put OPC as a prospective material for electrodes for EDLC applications. In addition to the excellent electrochemical features of OPC, it is worthwhile to observe that the source for the carbon is renewable and natural, obviously cost effective. Thus the study opens up avenues for the utilization of onion peel waste as a new carbon material for EDLC applications. One direction which further research can be undertaken would the investigation of activated carbon from the onion peel.

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