Study of correlation of structural and surface properties with electrochemical behaviour in carbon aerogels

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Carbon aerogel is a promising material for electrochemical double layer capacitors. In this paper carbon aerogels prepared by subcritical drying method are investigated for the change in the structure and surface properties at different pyrolysis temperatures. The important relations between structure, morphology, surface area and electrical properties were studied using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), surface area measurement and cyclic voltametry. It is shown that structure and the surface functional groups play important role in enhancement of electrochemical capacitance. The specific capacitance achieved was 114 F/gm which is quite large value for subcritically prepared carbon aerogels without any kind of activation process. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Supercapacitors are high power density electrochemical double layer capacitors with long life time [1–3]. They can be quickly charged and discharged with high energy efficiency. The electrical energy is stored in them mainly by non-faradaic processes (electrostatic charge separation at solid electrode and liquid electrolyte interface). There are also redox type supercapacitors where charging and discharging involve faradaic process, involving transfer of electrons between two phases. A good supercapacitor material should have a large specific surface area, high electrical conductivity, good mechanical, chemical and structural stability over a long period, so that it can be recycled many times without any faradaic reaction in the electrolyte.

Some of the important materials considered for supercapacitor application include carbon in various forms, metal oxides such as RuO_2, IrO_2, polymeric materials such as p- and n-dopable poly(3-arylthiopene), p-doped poly(pyrrole), poly(3-methyl thiophene), and (1,5)diaminoanthraquinone [4]. However, carbon is one of the most preferred material for fabrication of electrochemical double layer supercapacitors [5] because of its abundance in nature, chemical stability, large surface area and significantly stable potential window in a given electrolyte. Different forms of carbon like carbon powder [6, 7], carbon nanotubes [8], conducting polymers [9], activated carbons [10, 11] and aerogels [12–18] are studied for supercapacitor application. Amongst these, carbon aerogels are promising candidates for supercapacitors as these are highly porous, thereby having a large surface area and low electrical resistivity. More importantly, the surface area and pore size distribution can be easily tailored by controlling the chemical concentrations, temperature etc. during synthesis. In addition, the flexibility of preparing the aerogels in various shapes and sizes (monoliths, powders, thin films etc.) is an important factor in fabricating the electrodes.

The synthesis of carbon aerogels is known for last decade and conventionally these are prepared by pyrolysis of resorcinol formaldehyde (RF) aerogels [19–24]. There have been some attempts to measure the capacitance of carbon aerogels prepared by supercritical as well as subcritical drying method. High values of capacitance (95 F/g) are achieved for carbon aerogels prepared by supercritical drying method [15]. The reason behind this is larger surface area. However, supercritical drying step in the synthesis is very expensive and risky. It will be more useful from commercial aspects if carbon aerogels of high electrochemical preformance can be produced at low cost and by non hazardous method. Therefore here an attempt is made to study carbon

aerogels prepared by subcritical drying method. The highest capacitance achieved so far was 44 ± 2 F/cm^3 for carbon aerogels having a density of 0.54 g/cc, prepared by subcritical drying [18]. The corresponding specific capacitance was $\sim$81 F/gm. Here we report higher value i.e. 114 F/g. The values of capacitance can be enhanced by activating carbon aerogels either by heating in air or treating with nitric acid [19]. There is a lot of discussion about the effect of reaction conditions, pyrolysis temperature, surface area and mesoporous structure of carbon aerogels on electrochemical capacitance. However there are some additional aspects like structure and surface functional groups which also play an important role in the enhancement of capacitance in carbon aerogels about which there is very little discussion in the literature.

Supercapacitor material needs to be electrically conducting. It is reported here that the structural property decides the electrical conductivity in carbon aerogel. The double layer formation in capacitor is maximum when large surface area is accessible to the electrolyte. This mainly depends on the nature of surface functional groups. Therefore it is important to investigate structural and surface properties of carbon aerogels for supercapacitor application. In this paper we report the co-relation of surface and structural properties with the electrochemical capacitance for carbon aerogels prepared by pyrolysis of RF aerogels at various temperatures.

2. Experimental
Resorcinol (R), formaldehyde (F) and sodium carbonate (C) were used to synthesize RF aerogel as discussed in the literature [26]. Double distilled water was used as solvent. The R:F and R:C molar ratios were taken as 1:4 and 1:1000 respectively. The RF concentration was kept at 30 wt%. The mixture was poured into glass vials, which were sealed and gelation was carried out at 80°C. The aqueous gels were then exchanged with ethanol and dried subcritically. The RF aerogels thus prepared were then heated at various temperatures from 620 to 1150°C for 24 h in nitrogen atmosphere to convert into carbon aerogels.

The surface morphology of the aerogels before and after pyrolysis was analyzed using a Leica S-440 scanning electron microscope. Since, unlike carbon aerogels, RF aerogels are electrically insulating, they were coated with gold using a Poloron E5000 sputter-coating unit. Sputtering was done at 20 kV and 25 pA.

Surface area measurements were made using the Brunaur-Emmetet-Teller (BET) method with a Quantachrome NOVA 1200. Sample was heated to 300°C for three hours for removal of adsorbed gases before starting the measurements.

Powder X-ray diffraction (XRD) analysis was carried out using a Philips PW1840 diffractometer with Cu K$_\alpha$ source.

Fourier Transform Infrared (FTIR) spectra were recorded using a Perkin Elmer 1615 spectrometer using samples in the form of pellets made from crushed aerogel after mixing with spectroscopic grade KBr.

Cyclic Voltametry and impedance measurements were performed using 1M H$_2$SO$_4$ as an electrolyte. Monolithic carbon aerogel was used as the working electrode after measuring its weight accurately. The connection was made using copper wire. A platinum electrode was used as the counter electrode and Ag/AgCl electrode as reference electrode.

3. Results and discussion
The temperature of pyrolysis is an important parameter in preparation of carbon aerogels. The temperature was selected from Differential Thermogravimetry (DTG) and Thermogravimetry (TG) of RF aerogel (not shown here) where there was a change in the gradient of the weight loss at 600°C. In earlier reports the temperature used to prepare carbon aerogels was in the range of 600–2000°C [16, 26, 27].

It is observed that the density increased slightly with an increase in the pyrolysis temperature and this is shown in Fig. 1. For illustration, precursor RF aerogel is termed as sample A and carbon aerogels prepared at 620, 730, 900 and 1050°C are termed as sample B, C, D and E respectively.

SEM pictures of RF aerogel and carbon aerogel are shown in Fig. 2. The network in RF aerogel can be clearly seen in Fig. 2a. The particle diameter is in the range of 50–100 nm. The pore diameters are very big with a wide distribution ranging from 100 nm to 1 μm. Fig. 2b shows SEM for carbon aerogel (sample E) in which the pore diameter is comparatively small with narrower size distribution compared to RF aerogel. The particles are more compact and therefore more interconnected but the porosity is still retained. The surface area measured by BET technique was found to be 500 m^2/gm for sample E. This result is comparable with those reported by Pekala earlier [16].

The changes in the structure of carbon aerogel with increase in the pyrolysis temperature were investigated using XRD. Fig. 3a–e shows XRD spectra for sample A to E respectively. Broad peaks are observed at $2\theta = 25°$ and $34°$ in the RF aerogels (Fig. 3a). These peaks can be attributed to amorphous carbon. The graphs b and c show the peaks at $2\theta = 23°$ and $43°$ and in the remaining graphs the peaks appear at $24°$ and $44°$. The FWHM of
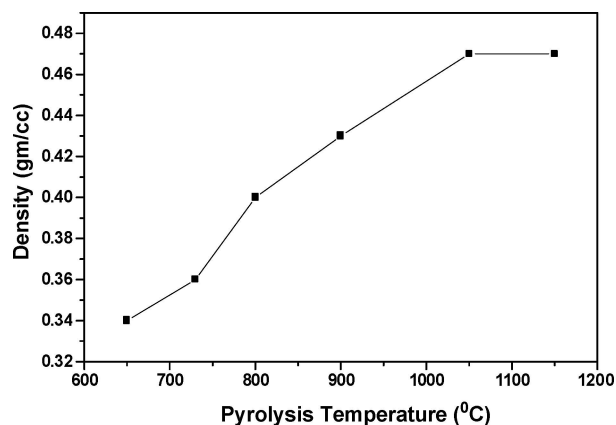

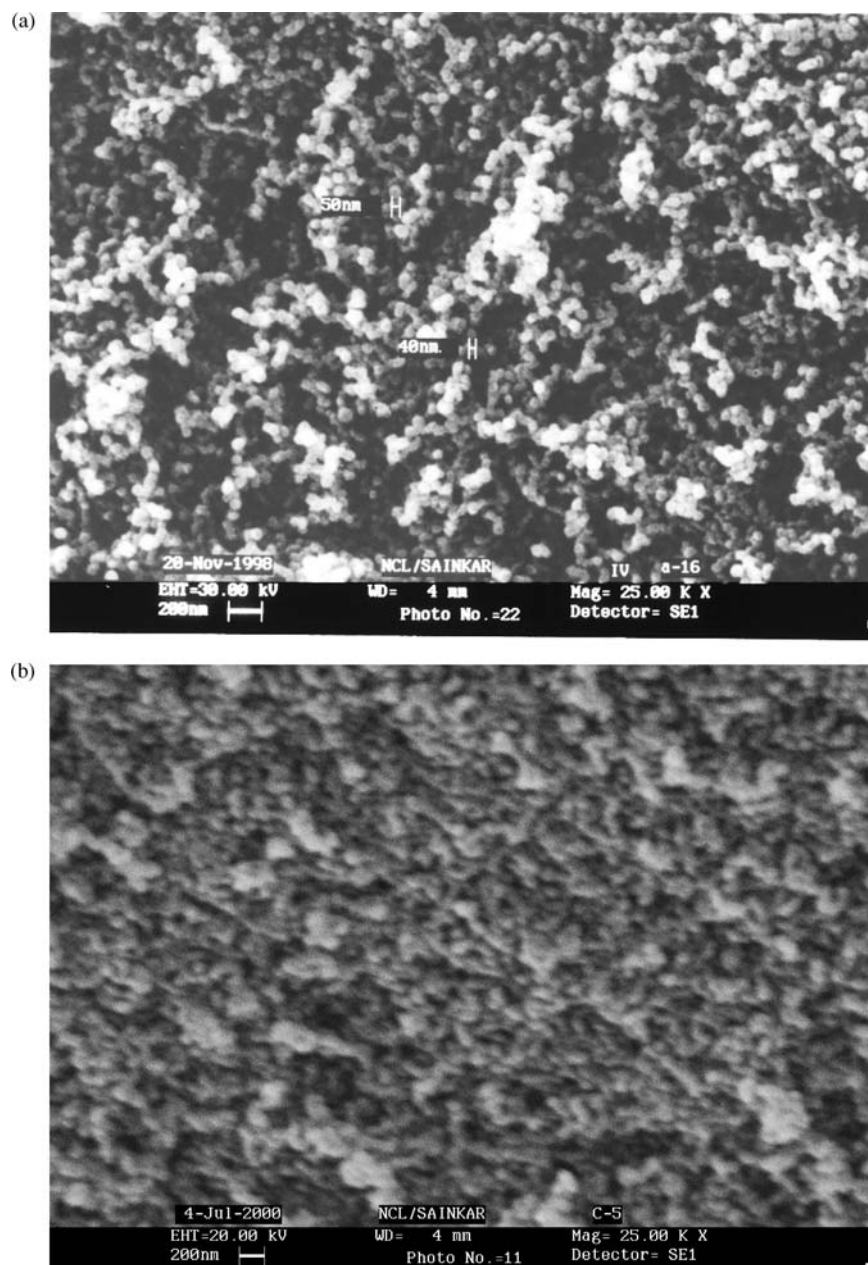*Figure 1* Change in the density of carbon aerogel with pyrolysis temperature.

Figure 2 (a) SEM of RF aerogel (b) SEM of carbon aerogel (sample E).

the most intense peak in spectra a, b, c, d and e decreases with pyrolysis temperature as shown in inset of Fig. 3. The peaks for carbon aerogels are comparatively less broad. The peak at 44° also becomes more prominent as the pyrolysis temperature is increased. The interplanar distance (d_{111}) for graphite is 0.335 nm. The calculated value of d_{111} for samples B and C is 0.393 nm. For samples D and E, it is 0.364 nm. It can be seen that as the pyrolysis temperature increased, the 'd' value started approaching that of pure graphite. Although the XRD spectra D and E are similar, there is a difference in the densities as shown in Fig. 1.

The FTIR spectra were recorded to understand the changes in the functional groups present on the surface while converting RF aerogels into carbon aerogel at various temperatures. Fig. 4 a–e shows FTIR spectra for sample A to E respectively. FTIR spectrum for RF aerogel (Fig. 4a) is in good agreement with literature [26]. The broad peak at 3424 cm^{-1} can be attributed

mainly to the –OH groups bonded to the benzene ring but also may be due to –CH$_2$OH groups connected to the resorcinol molecule, which did not take part in network formation. The peaks at 2925 and 1480 cm^{-1} are attributed to stretching of –CH$_2$ groups and 1614 cm^{-1} peak is due to aromatic ring stretching. The peaks observed at 1091 and 1220 cm^{-1} confirm the C—O—C linkage stretching between two resorcinol molecules, which is expected in the polycondensation reaction between resorcinol and formaldehyde.

When RF aerogel is heated at 620°C, the nature of FTIR spectrum totally changes (spectrum b). The intensity of the broad peak at 3424 cm^{-1} gets reduced and new small peak appears at 3544 cm^{-1}. This can be correlated to the primary OH groups. This peak becomes dominant as the heating temperature increased from 620 to 900°C. For 1050°C it became very sharp. This means that the number of primary or free OH groups increases with an increase in temperature. Because of
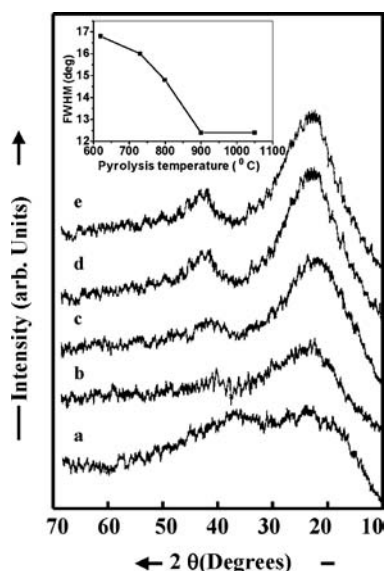
Figure 3 XRD for (a) RF aerogel and carbon aerogels prepared at (b) 620°C; (c) 730°C; (d) 900°C; (e) 1050°C.
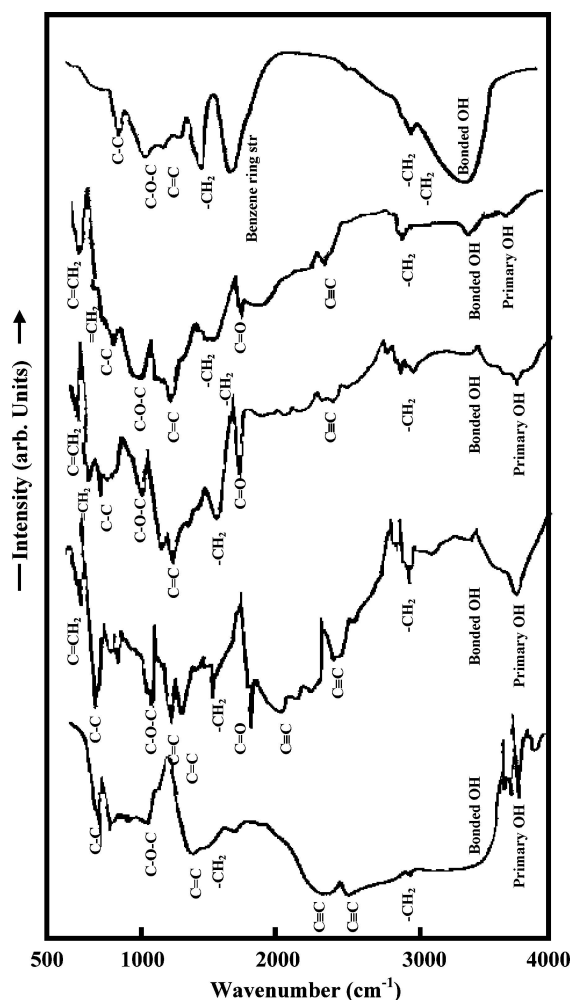

Figure 4 FTIR of RF aerogel (a) and carbon aerogels prepared at (b) 620°C; (c) 730°C; (d) 900°C; (e) 1050°C.

heating, some of the CH_2-O-CH_2 linkages may have broken to form $-CH_2OH$ and $=CH_2$ groups attached to different resorcinol molecules. This is further supported by the sharp intense peaks observed in sample B, C, D at 550 cm^{-1} and 660 cm^{-1} due to the C$=CH_2$ groups not seen in sample E. These peaks are absent

in case of RF aerogel. But some CH_2-O-CH_2 links are intact, as peaks at 1091 and 1220 cm^{-1} are still present for all other samples. The small peak at 2925 cm^{-1} in the spectrum of the RF aerogel is due to the C$-$H stretching vibrations. The intensity of this peak (which is absent in sample E) increased for samples B, C, D. The peak at 1614 cm^{-1} for aromatic stretching is absent in sample B, C, D and E. Peaks observed at 2398 and 2204 cm^{-1} can be attributed to $-$C$\equiv$C$-$. This means that the benzene rings are broken while heating and $-$C$\equiv$C$-$ bonds are formed at the broken ends. The peak at 1488 cm^{-1}—due to C$=$C$-$ is present in all samples. A new peak at 1744 cm^{-1} can be seen only in the sample B, C and D. This can be attributed to C$=$O group. This group may be either from carboxylic (COOH) group or the quinone group, which may be formed at the broken C$-$O$-$C linkages in the presence of oxygen. Heating above 900°C removes this group in case of sample E. The peaks at 840, 751 and 570 cm^{-1} are also present in all samples. But in sample A, these are not resolved. These peaks can be due to C$-$C vibrations. Thus, it can be infered that as the temperature of heating increased the carbon aerogels became more hydrophilic due to the formation of more free OH groups. Also the benzene ring breaks during heating to form aliphatic carbon. At temperature lower than 1050 cm^{-1}, C$=$O groups are observed. No FTIR spectrum for carbon aerogels has been reported in earlier literature.

Fig. 5 shows the change in the resistance and capacitance of the carbon aerogels with a change in the pyrolysis temperature. As the heating temperature increased from 620 to 1150°C, the resistance dropped from 16 MΩ to 6.5 Ω. This can be understood from the change in the XRD pattern which suggests the formation of graphite like carbon with increase in pyrolysis temperature. The amorphous carbon in RF aerogel changes its nature and carbon from sample E shows resemblance to the graphite like structure. This in turn results into lowest resistance sample amongst all these samples.

The electrochemical behavior of the carbon aerogels was characterized by the cyclic voltametry. The capacitance of the aerogels was calculated using $C = i/v$, where i (mA) is the current in the linear region of the voltammograms, which is relatively constant over the capacitive voltage window and v is the applied scan rate in mV/s.
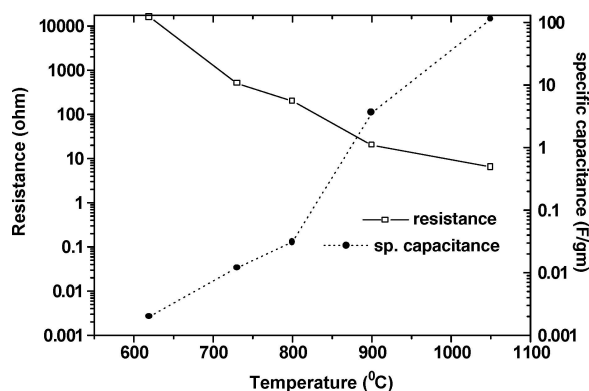

Figure 5 Change in the resistance and specific capacitance with pyrolysis temperature Log scale on *Y* axis.
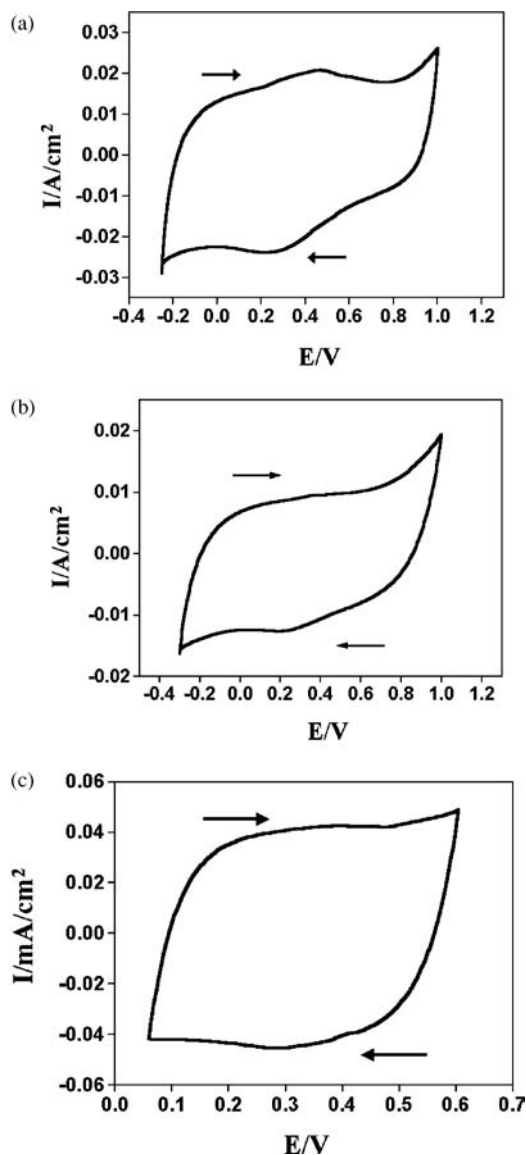
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Figure 6 Cyclic Voltametry carbon aerogel (E) prepared at 1050°C. Scan rate used was 500 mV/sec (a) after 1 cycle (b) after 30 cycles and (c) after 50 cycles.

Figure 7 Impedance spectrum of carbon aerogel (E) prepared at 1050°C.

Aerogels prepared in the temperature range 620–900°C exhibit a lower value of gravimetric capacitance as compared to that of aerogels heated at 1050°C. This variation in capacitance can be ascribed to the different conductive percolation networks developed in the aerogels at different pyrolysis temperatures. Higher pyrolysis temperature (1050°C) decreases the specific volume (reciprocal density) of the aerogel making it denser to form an interconnected network of carbon nanoparticles as also seen from SEM. This network presents a uniform mesoporous microtexture with a specific surface area of 500 m^2/g, which is the origin of the large capacitance.

Fig. 6a displays the cyclic voltamogram of an aerogel (E) in 1 M H_2SO_4 at a scan rate of 10 mV/s. An immediately apparent feature is that the aerogel shows an ideal capacitative behavior resulting in an almost rectangular voltamogram. The presence of ill-defined peaks around 0.46 and 0.21 V (vs. Ag/AgCl) can be ascribed to oxygenated surface functional groups such as carbonyl and phenolic one that are formed because of surface oxida-
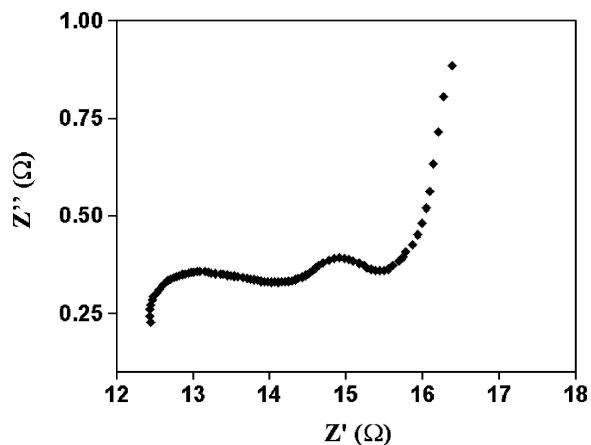
tion, the presence of which is confirmed from FTIR studies. The nature of the voltamogram changes with increasing number of cycles. The pseudocapacitive behavior associated with these functional groups diminishes after continuous cycling due to the irreversibility of the redox reactions. Fig. 6b shows a stable, nearly perfect rectangular cyclic voltammogram after 30 cycles where there are no redox peaks. Fig. 6c shows a stable, perfectly rectangular cyclic voltammogram after 50 cycles that shows a specific capacitance of 114 F/g.

Impedance measurements provide a complementary evaluation of a capacitor in addition to cyclic voltametry. All the measurements were carried in the frequency range 0.01 to 100 kHz employing an ac signal with an amplitude of 5 mV. The electrolyte was 1 M H_2SO_4 for all experiments.

Fig. 7 shows an impedance spectrum of an aerogel (E). For the convenience of interpretation, the plot can be divided into high frequency region and low frequency regions. The high frequency region shows the presence of two semicircles, which have resulted from the solution resistance and the charge transference resistance within the porous structure. The frequency at which there is a deviation from the semicircle is known as 'knee frequency', which reflects the maximum frequency at which capacitive behavior is dominant. The lower frequency region exhibits a vertical line that starts at an angle of 45° approaching an almost vertical line at lower frequencies, thus showing an ideal capacitor behavior. Any deviation from ideal behavior can be attributed to the distributions of charge transfer rates, adsorption processes or surface roughness. The capacitance of the electrode structure is calculated by the equation $Z'' = 1/j\omega C$ (Z'' = imaginary component of an impedance; ω = angular frequency; C = capacitance and j = complex number) which is 4.5×10^{-3} F.

On correlating the data from density measurement as a function of pyrolysis temperature, SEM, XRD, FTIR and electrical measurements we can infer the following. As the pyrolysis temperature increases, carbon becomes more graphitic and the particles come closer to form a network, increasing the connectivity between them. This results in the carbon aerogels having higher electrical conductivity. The FTIR study showed that the number of primary OH groups goes on increasing

with temperature. These groups make the aerogel more hydrophilic. The electrochemical capacitance measurement is done in aqueous sulphuric acid. When the aerogel electrodes are dipped in the electrolyte, the surface area where electrolyte has reached will form the double layer. It is possible that electrolyte cannot reach some of the smaller pores at the core of the sample. The OH groups increase the double layer formation and therefore the capacitance also increases. We also suggest that C=O groups present in sample B, C, D and E may contribute to higher capacitance. The high capacitance of sample C appears to have resulted from its low resistance, higher particle connectivity and the presence of C=O group as well as higher number of primary OH groups.

Thus, low density, high surface area and highly conducting carbon aerogels can be prepared by following the subcritical drying route. The information generated from the combination of techniques suggests that the structure of aerogels before and after pyrolysis is totally different. Efforts are being made to dope these carbon aerogels with ruthenium dioxide to combine the advantages of faradaic and non-faradaic capacitance to further increase the specific capacitance.

4. Conclusion

The carbon aerogels prepared using higher R:C molar ratio, subcritical drying and pyrolysis at 1050°C show several superior features which lead to higher values of capacitance. The capacitance increased with an increase in the pyrolysis temperature. The combined effect of higher surface area, higher particle connectivity, low resistance and the presence of surface functional groups gave a high specific capacitance of 114 F/gm, which is quite a larger value for subcritically dried carbon aerogels without any kind of activation process.

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