Electrochemical behavior of amorphous carbon obtained from camphor

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Abstract

Amorphous carbon films were deposited on alumina plate by pyrolysing camphor at different temperatures with thermal chemical vapor deposition (CVD) technique. Carbon coated alumina plates were used as working electrode to ascertain their electrochemical behavior in different electrolytic media. Electrochemical windows of these carbon films were found to be suitable in the potential range of 1.05 to -0.30 V versus SCE in acid medium. In the presence of redox electrolyte, cathodic–anodic peak separation was found to be the same as that obtained with diamond. Raman spectra of carbon films were studied to explain some of their electrochemical behavior.
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1. Introduction

One of the most commonly used electrodes is platinum. Boron doped diamond (BDD) is another very promising material for electrochemical studies due to its wide potential window in aqueous [1–3] and non-aqueous [4,5] media. At the same time, diamond film is found to be electrochemically much stable [6,7]. Wastewater treatments, oxidation of alcohol and acids are some new fields of science where boron doped diamond electrode have been used [8–10]. Some of the recent reports show different aspects and use of boron doped diamond electrode in electro analysis [11–15]. Both, platinum and natural diamond are costlier materials. Synthesizing artificial diamond and boron doped diamond film needs sophisticated instruments, which restricts the use of diamond as an electrode up to some extent. However, electrochemical studies of diamond-like carbon (DLC) mixed with platinum have been reported by Pleskov et al. [16]. Electrochemical

characterizations of graphite, glassy carbon and carbon paste as inert electrodes are also being done. The drawback with graphite is that when used for a longer time it produces carbon dust in the electrolyte. Therefore, electrochemists are searching for electrodes that are economical, non-corrosive, stable, chemically and electrochemically inert. There are very few studies performed on the electrochemical behavior of amorphous carbon films [17] and these films are dissimilar to DLC and glassy carbon. Amorphous carbon films can be easily deposited on a large surface without using sophisticated instrument.

The electrochemical stability of polycrystalline diamond films and amorphous DLC films is higher than the graphite due to the incorporation of sp^3 carbon in the lattice of carbon. Polycrystalline diamond and amorphous DLC films are synthesized with different deposition technique using methane, acetone, etc. as a precursor in presence of hydrogen gas [18,19]. The resulting diamond is an insulator and cannot be used for electrochemical studies. So either it has to be heavily doped by boron/phosphorous or to be incorporated by sp^2 carbon to make it electrically conducting. Conventional method of synthesizing diamond films demands very stringent conditions to prepare large sized films. Therefore

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simpler technique and cheaper carbon precursor are needed for the synthesis of carbon films having properties similar to that of DLC and yet easy to grow on large size substrates for the industrial applications.

We report here the electrochemical properties of amorphous carbon thin films deposited on alumina plate by pyrolysis of camphor, a natural hydrocarbon precursor. Cyclic voltammetry was performed with different carbon films in all three, i.e. redox, acidic and basic media. Raman studies were carried out to find the nature of carbon films.

2. Experimental

A dual furnace was used for the deposition of carbon on alumina plate by thermal CVD method. Detailed experimental set-up is reported elsewhere [20]. First furnace was used for the vaporization of hydrocarbon precursor, i.e. camphor and in the second furnace, pyrolysis was carried out at different temperatures. Carbon films were deposited on alumina plate by pyrolysis of camphor at different temperatures in a nitrogen atmosphere. XRD analysis suggested that these films were made of amorphous carbon. This film henceforth is referred as carbon electrode.

Electrochemical studies of carbon films were done in a three-electrode single compartment electrochemical cell, one of them is a large area counter electrode of platinum and the other is saturated calomel electrode (SCE) as a reference. This study was made to observe whether these carbon electrodes could be used for electrochemical studies instead of platinum or diamond. Cyclic voltammetry (CV) investigation was carried out in three different electrolytes: (i) 100 mM H_2SO_4, (ii) 100 mM NaOH and (iii) 100 mM $K_4Fe(CN)_6 \cdot 3H_2O + 10$ mM $K_3Fe(CN)_6$. The redox electrolyte 100 mM $K_4Fe(CN)_6 \cdot 3H_2O + 10$ mM $K_3Fe(CN)_6$ was used, as it gives good oxidation and reduction peak in CV with platinum and many reports are available with various form of carbon electrode. The cyclic voltammetry was recorded by a computer programmed interface device using a Bio-Potentiostat (model AFRDE4). The effect of scan rate on the anodic and cathodic currents was also studied.

3. Results and discussion

The electrochemical potential windows of camphor pyrolysed carbon in contact with H_2SO_4 and NaOH solutions were investigated in the potential range of −1.5 to 2.5 V versus SCE at different scan rates. The same experiment was repeated with platinum and graphite electrode using Pt as counter electrode. During entire experiment, geometry of cell and exposed area of all the working electrodes were kept constant. Fig. 1(a) shows cyclic voltammograms (CVs) of carbon film obtained at pyrolysis temperature of 900 °C exposed to 100 mM H_2SO_4 solution. CV of carbon films prepared
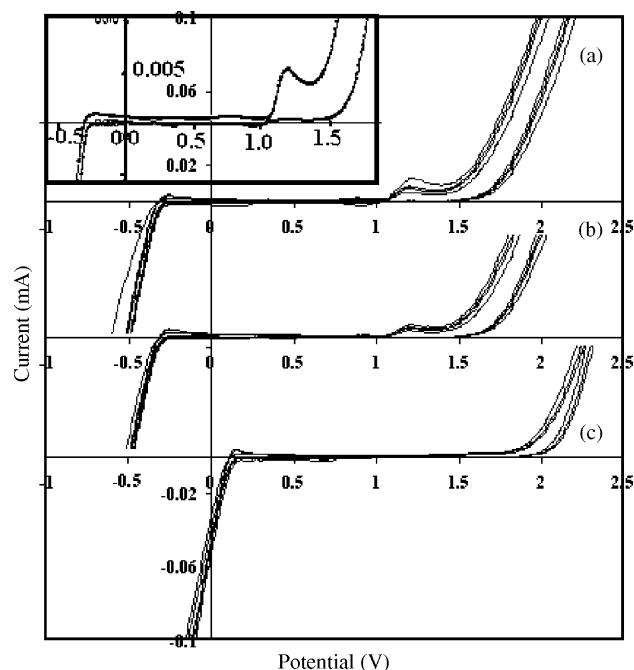

Fig. 1. Cyclic voltammograms of: (a) carbon film obtained at a pyrolysis temperature of 900 °C; (b) graphite; (c) platinum; with Pt as counter electrode exposed to the electrolyte (100 mM H_2SO_4) at a scan rate of 25, 50, 75 and 100 mV (reference electrode: SCE). (Inset shows the clear behavior of a representative CV curve of carbon electrode at low current scale.)

at other pyrolysis temperature was almost same type. For comparison, CV of platinum and graphite was taken in the same acid concentration. Fig. 1(b) and (c) shows the CV plot of cell configuration "graphite/100 mM H_2SO_4/SCE/Pt" and "Pt/100 mM H_2SO_4/SCE/Pt", respectively, at different scan rates. The potential window of carbon electrodes were found to be almost same as that obtained with platinum whereas smaller than diamond electrode ($\sim$2.5 V) [10]. However, carbon electrode obtained from pyrolysis of camphor has a better edge over platinum especially in the potential range of 0.13 to −0.30 V versus SCE. Although graphite electrode showed similar behavior but this being unstable in acidic and alkaline medium, amorphous carbon electrode prepared at much lower temperature to graphite is favored. It is interesting to note that there was no major change in the potential window of amorphous carbon electrode prepared at different pyrolysis temperatures (Table 1).

Table 1

Electrochemical potential windows of various inert electrodes as observed in 100 mM H_2SO_4 solution

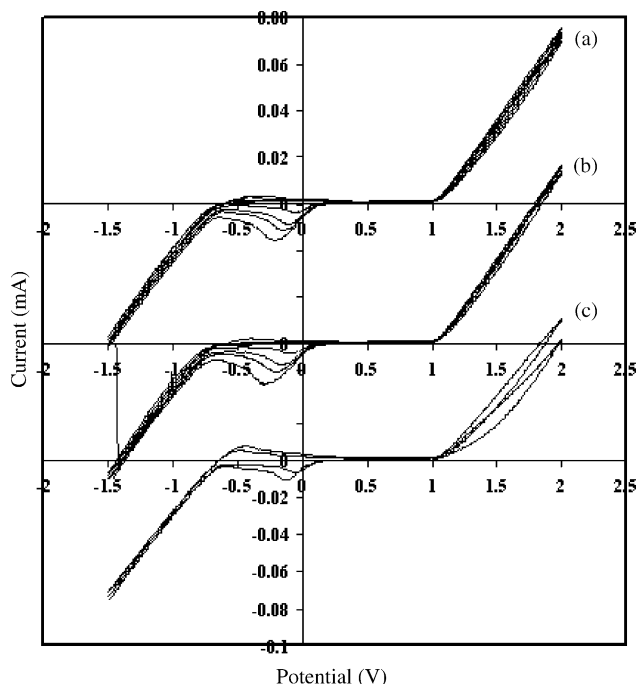| Working electrode	Counter electrode	Window (V)	Range of windows (V)
Carbon electrode (900 °C)	Pt	1.35	1.05 to −0.30
Carbon electrode (1000 °C)	Pt	1.39	1.05 to −0.34
Carbon electrode (1100 °C)	Pt	1.4	1.06 to −0.34
Carbon electrode (1200 °C)	Pt	1.38	1.05 to −0.33
Graphite	Pt	1.37	1.06 to −0.31
Platinum	Pt	1.39	1.52–0.13

Fig. 2. Cyclic voltammograms of: (a) carbon obtained at a pyrolysis temperature of 900 °C; (b) graphite; (c) platinum; with Pt as counter electrode exposed to the electrolyte (100 mM NaOH) (scan rate for: (a) and (b) 25, 50, 75 and 100 mV; (c) 50 and 100 mV).

Fig. 2(a) shows the CVs of camphor pyrolysed carbon obtained at 900 °C in an alkaline (NaOH) medium. A cathodic reduction peak was observed in the potential range of 0 to −0.6 V. Similar type of peak was observed when graphite and platinum electrode were used in combination with platinum as counter and SCE as a reference electrode in 100 mM NaOH solution at different scan rates (Fig. 2(b) and (c)). This cathodic peak therefore may be due to some impurities present in the NaOH solution like carbonate ions. The nature of CV curve of amorphous carbon electrode prepared at other pyrolysis temperature (1000, 1100 and 1200 °C) was found similar. It can be assumed that the potential windows as well as the range of potential are almost same for all these electrodes, suggesting that carbon electrode obtained from the pyrolysis of camphor can be used safely in this potential range.

The electrochemical behavior of these carbon films obtained at different pyrolysis temperature was also studied in 100 mM $K_4Fe(CN)_6 \cdot 3H_2O + 10$ mM $K_3Fe(CN)_6$. Fig. 3(a) shows typical CVs of carbon film obtained at 900 °C with Pt counter and SCE reference at different scan rates. Fig. 3(b) shows a CV plot of carbon films obtained at different pyrolysis temperatures and graphite versus Pt working electrode at a scan rate of 100 mV/s. Fig. 3(c) shows a CV of platinum as working electrode to Pt counter at a scan rate of 100 mV/s for comparison. As seen from the figure, the current produced by amorphous carbon, graphite and platinum electrode was almost identical. This investigation reveals that the reactivity of as-grown carbon electrode was comparable to that of plat-
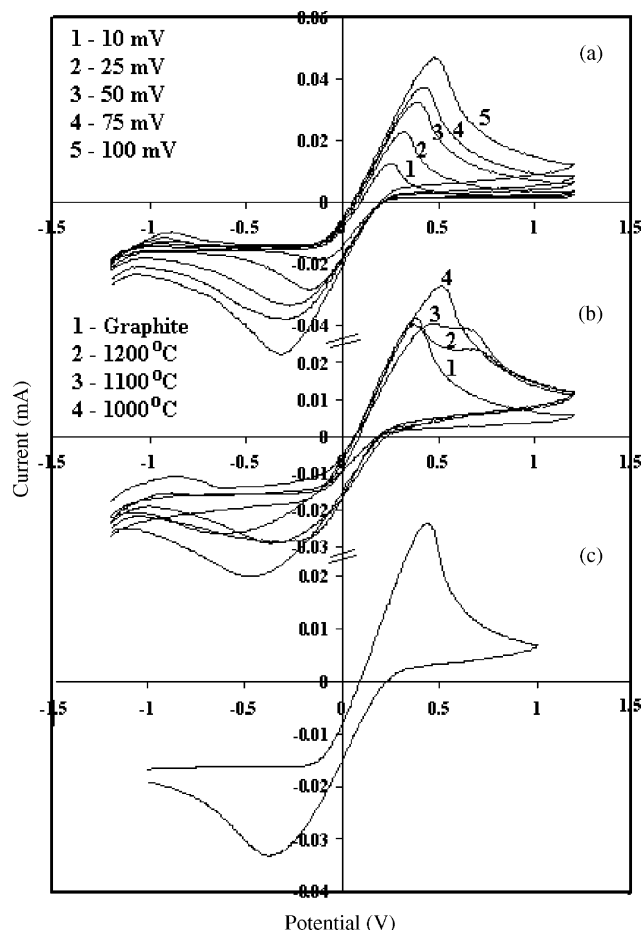

Fig. 3. (a) CV of carbon film obtained at a pyrolysis temperature of 900 °C with Pt as counter electrode in 100 mM $K_4Fe(CN)_6 \cdot 3H_2O + 10$ mM $K_3Fe(CN)_6$ at a scan rate of 10, 25, 50, 75 and 100 mV; (b) CV of carbon film obtained at a pyrolysis temperature of 1000, 1100 and 1200 °C and graphite at a scan rate of 100 mV; (c) CV of platinum with Pt as counter electrode in 100 mM $K_4Fe(CN)_6 \cdot 3H_2O + 10$ mM $K_3Fe(CN)_6$ at a scan rate of 100 mV.

inum electrode. A similar study was also reported by Zhu et al. for the boron doped diamond films grown by CVD, but their CVs were poorly defined, reflecting slow reaction kinetics, may be due to higher resistance of the electrodes [21]. However, it should be mentioned here that the resistivity of these materials are not in the same range. Table 2 presents the room temperature resistivity of carbon electrode prepared in this study. Carbon electrode prepared at lower temperature

Table 2
Room temperature resistivity of carbon electrode prepared at different pyrolysis temperatures

Preparation temperature (°C)	Resistivity (Ω m)
900	0.21×10^{-4}
1000	0.45×10^{-6}
1100	0.39×10^{-6}
1200	0.12×10^{-6}
BDD	$\sim 10^{-4}$
Glassy carbon	$\sim 10^{-6}$
Pt	$\sim 10^{-8}$

has a resistivity closer to boron doped diamond films whereas other electrodes have resistivity closer to glassy carbon electrode. The resistivity of the carbon electrode decreases with the temperature due to increase in disorderliness and sp^2 carbon in the films prepared at higher temperature. Due to complexity in the percentage of sp^3/sp^2 carbon, disorderliness and dopants in the films of carbon it is not easy to compare the behavior of different carbon electrode to platinum. Moreover, it has been widely accepted that boron doped carbon electrode and other carbon electrode can be used for many electrochemical studies.

The electrochemical behavior of as grown carbon films in the aforesaid redox electrolytes were investigated at scan rates of 10, 25, 50, 75 and 100 mV/s and the anodic peak currents were plotted against the square root of scan rate. The response current was found to increase linearly with the square root of the scan rate. A typical plot is shown in Fig. 4. As-obtained straight lines indicate diffusion-controlled electrode reactions at the carbon surface, similar to those obtained with Pt electrode.

The degree of reversibility of an electrochemical reaction can be judged qualitatively from the potential difference (ΔE_p) for the cathodic and anodic current peaks. The higher the ΔE_p (the wider the current peak separation along the potential axis), the more irreversible is the reaction [22,23]. Anodic–cathodic peak separations (ΔE_p) for this redox system were found to be 800, 960, 1080 and 600 mV for the carbon films prepared at temperatures 900, 1000, 1100 and 1200 °C, respectively, at a scan rate of 100 mV/s (Table 3). Two types of electro-catalytic sites were observed in the case of carbon electrodes obtained at a pyrolysis temperature of 1100 and 1200 °C, which makes the peak separation voltage measurement more complicated. The origin of new peak is unknown but it may be related to the electrochemical activity of non-diamond carbon formation at higher pyrolysis temperature, which was clear from the resistivity measurement. Electrodes prepared at higher pyrolysis temperature
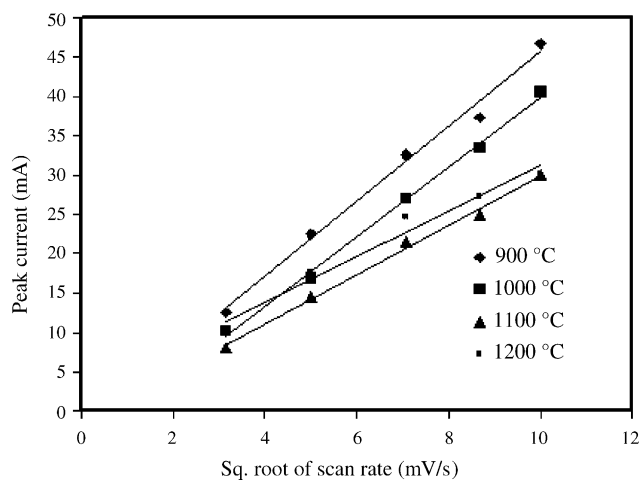
Table 3
Comparison of peak separation voltage obtained from different carbon films

Working electrode	Counter electrode	ΔE_p (mV)
Carbon films obtained at 900 °C	Pt	800
Carbon films obtained at 1000 °C	Pt	960
Carbon films obtained at 1100 °C	Pt	1080
Carbon films obtained at 1200 °C	Pt	600
Graphite	Pt	760
Platinum	Pt	840

were more conducting in nature (Table 2). However, there was an increase in the peak separation with carbon electrodes prepared at 900–1100 °C and then significant decrease of ΔE_p for the electrodes prepared at 1200 °C if we consider the first anodic peak. This is due to the increase in the disorderliness in the carbon films with increase of pyrolysis temperature, which is clear from the Raman studies (discussed later) and then decrease of disorderliness at the higher temperature (1200 °C) due to the formation of more graphitic carbon. Fig. 5 shows the dependence of anodic and cathodic peak potential versus logarithm of scan rate, which is found to be linear, as also obtained by Pleskov et al. for narrow band gap amorphous carbon material [17].

The transfer coefficient α and exchange currents density were obtained from the Tafel plots (Fig. 6) and is given in Table 4 for the carbon electrodes obtained at different pyrolysis temperatures [23]. The poor linear portion of the curves was very narrow (0.15–0.25 V) and this may be due to diffusion-controlled electrode reactions. Exchange current densities obtained from electrodes prepared at different pyrolysis temperature and platinum were of same magnitude. This indicates that electrochemical activity of these electrodes is as good as platinum. Kinetics of electrochemical reaction can also be related to the peak separation value (ΔE_p). Since ΔE_p in our case is more than 200 mV, the Nicholson's approach for calculation of the apparent rate constant is ruled out [24,25].

Fig. 4. Current response of camphoric carbon films in 100 mM $K_4Fe(CN)_6 \cdot 3H_2O + 10$ mM $K_3Fe(CN)_6$ against square root of scan rate.
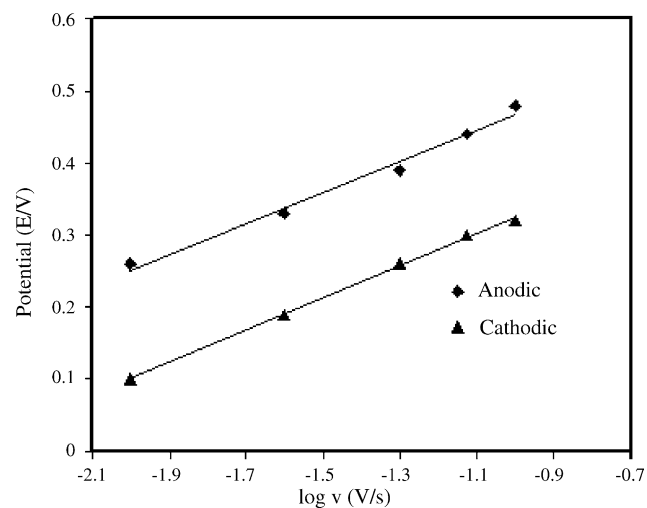
Fig. 5. Dependence of anodic and cathodic peak potential on the logarithm potential scan rate of the carbon films obtained at 900 °C.
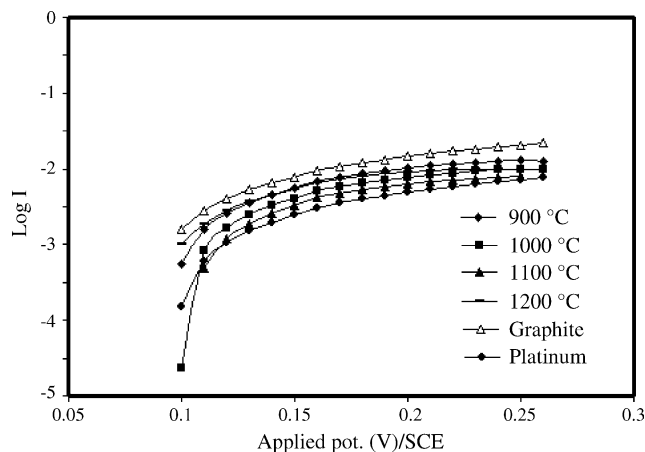
Fig. 6. Tafel plots for the oxidation of ferro- to ferricyanide at different carbon electrodes at 300 K having potential scan rate of 10 mV/s. α values were calculated from slope of all the curves and given in Table 3.

Fig. 7. Raman spectrum of carbon films obtained at: (a) 900 °C; (b) 1000 °C; (c) 1100 °C and (d) 1200 °C.

However, if we compare ΔE_p versus calculated rate constant qualitatively, the apparent electron transfer with the electrode obtained at 900 and 1200 °C is high. But electrodes prepared at a pyrolysis temperature of 1200 °C have not shown larger voltammetric peaks compared to electrode prepared at 900 °C. Thus, the single, sharper and larger voltammetric peaks along with lower ΔE_p makes the electrode prepared at 900 °C better than other electrodes studied in this work. To find the detail nature of carbon films Raman spectra were taken.

Raman spectra have been used extensively to get information about disorderliness, percentage of sp^3 and sp^2 carbon in the films. It is widely known that the first order sharp Raman peak of diamond and graphite lies at 1332.5 ± 0.5 and $1580 \pm 0.5\,cm^{-1}$, respectively. All other types of carbon show broad peaks between 1340 and 1600 cm^{-1} [27,28]. These two bands are also observed in amorphous carbon films and glassy carbon [29–31]. Moreover, it has been seen that the intensity of the D-band is higher in glassy carbon than the G-band in most of the cases so far reported [27,28,32]. Fig. 7 shows the Raman spectra of carbon films obtained at different pyrolysis temperatures. In the present study, two broad bands/peaks were observed at 1350 cm^{-1} (D-band) and 1580 cm^{-1} (G-band). Comparison of intensity of Ra-

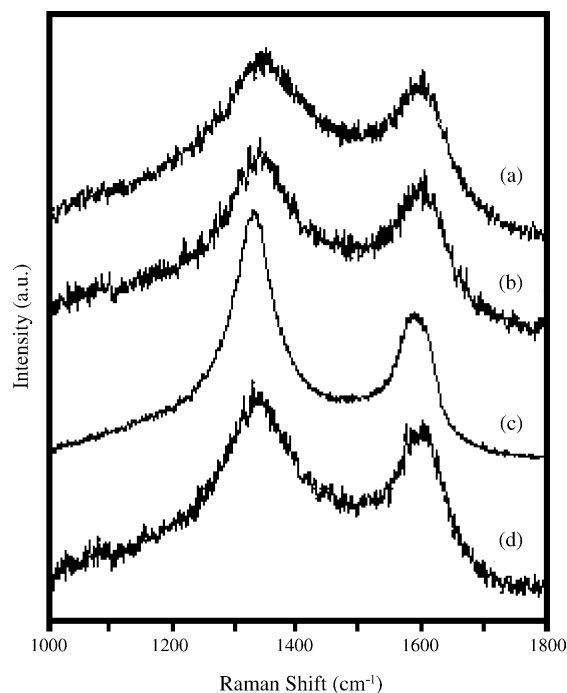man spectra of camphor pyrolysed films with that published by Kalish et al. [29,33] suggests that our film contains about 60% sp^2. It is well known that, with the increase in pyrolysis temperature there is an increase in disorderliness along with sp^2 carbon in the carbon films. Increase in disorderliness is measured from the increase in the peak ratio of D-band to G-band intensity (I_D/I_G). In the present case, there was an increase in I_D/I_G ratio (disorderliness) with increase of pyrolysis temperature from 900 to 1100 °C and then its sharp decrease at 1200 °C. The decrease of I_D/I_G at 1200 °C indicates the decrease in the disorderliness in the amorphous carbon films and increase of sp^2 carbon. This structural change in the films can also be compared with the anodic–cathodic peak separations (ΔE_p) value obtained in redox electrolyte. The decrease of ΔE_p at 1200 °C was due to the decrease in the disorderliness of carbon films and increase of sp^2 carbon. So, the disorderliness in the carbon films was the reason for poor reversible nature of carbon films deposited at 1100 °C whereas at 1200 °C, higher percentage of sp^2 along with some disorderliness makes the electrode poor reversible. It indicates that, carbon films prepared at pyrolysis temperature lower than 900 °C may show better reversible character. Moreover, films prepared at lower temperature possess high resistance. Hence, unless they are doped to reduce resistance, they may not be useful for electrochemical study. Therefore, percentage of sp^2 and sp^3, conductivity of the electrode, etc. plays main role for showing good electrochemical behavior and there is a need to investigate these behaviors in detail to find best amorphous carbon film electrode.

Table 4
Exchange current densities and transfer coefficient of carbon electrodes prepared at different pyrolysis temperatures

Pyrolysis temperature (°C)	Exchange current density	Transfer coefficient (α)
900	5.6×10^{-4}	0.61
1000	3.9×10^{-4}	0.64
1100	1.9×10^{-4}	0.58
1200	5.6×10^{-4}	0.64
Graphite	6.3×10^{-4}	0.64
Platinum	1×10^{-4}	0.53
Platinum [26]	0.2×10^{-4}	

4. Conclusions

Conducting carbon films were deposited by the pyrolysis of natural precursor camphor at different temperatures in a nitrogen atmosphere and their electrochemical behavior was studied in different electrolytic media for the first time. Electrochemical windows of amorphous carbon films were found to be suitable in the range of 1.05 to −0.30 V versus SCE in acid medium. In presence of redox ferro/ferricyanide electrolyte, peak separation was found to be the same as that obtained with diamond. The linear plot of current response versus square root of scan rate indicated a diffusion-controlled reaction at the surface of carbon. Comparing carbon films prepared at different temperature, it was observed that, carbon film deposited at 900 °C shows better reversible character. Since carbon electrode preparation from camphor by CVD technique takes few minutes and its electrochemical behavior is as good as graphite with its electrochemical window has an edge over platinum, this electrode can be safely used for many electrochemical works in the potential range of 1.05 to −0.30 V versus SCE in acidic medium.

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