A comparative evaluation on the voltammetric behavior of boron-doped diamond (BDD) and glassy carbon (GC) electrodes in different electrolyte media

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ABSTRACT

Voltammetric responses of boron-doped diamond (BDD) and glassy carbon (GC) electrodes on the anodic oxidation of two dissimilar compounds namely 2,6-dimethoxyphenol and 1,3,5-trimethylbenzene in acidic, neutral and basic media have been explored. Cyclic voltammetric (CV) analysis reveals that the BDD electrode shows wider cathodic potential window and lower background current in all the media than the GC. However, in the anodic side, the window is wide only in aqueous acidic medium and the background limit for both the electrodes is similar in both neutral and alkaline media containing solvents other than water. Further, the anodic oxidation of 2,6-dimethoxyphenol takes place at less potential on the GC when compared to the BDD and the oxidation peak current is also higher on the former electrode. CV results show that no anodic peak appears for the oxidation of 1,3,5-trimethylbenzene on the GC electrode in any of the above media, whereas in the acidic medium, a broad anodic wave appears on the BDD.

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1. Introduction

In recent years, boron-doped diamond (BDD) electrodes are being evaluated for potential applications in three major areas of research such as waste water treatment, electrosynthesis and electroanalysis. The advantages and supremacy of the BDD over the glassy carbon (GC) electrode in waste water treatment have been already established by a number of studies during the past two decades [1]. For example, extensive research works on the electrochemical degradation of substituted phenols [2], organic acids [3], dyes [4], herbicides [5], metabolites [6] and endocrine-disrupting chemicals [7] have been documented in the literature. Such electrochemical degradations take place on the BDD via intermediation of hydroxyl radicals, generated from the discharge of water along with concomitant oxygen evolution [8]. The presence of sp^3 carbon functionalities may lead to an inert surface with low adsorption properties and a strong tendency to resist deactivation. Further, there are only a few reports available in the literature related to the selective electro organic synthesis using the BDD electrode [9].

Applications of the BDD based sensors in electroanalysis of organic compounds have also been explored recently [10]. High stability, even in corrosive acidic fluoride media [11], low adsorption of organic compounds on the electrode surface [12], wide potential window [13] and low background current [14] have been claimed technologically important features that distinguish the BDD from conventional electrodes such as GC and highly oriented pyrolytic

graphite (HOPG). Furthermore, the voltammogram of organic compounds with high oxidation potentials exhibited higher S/B ratios with improved electrocatalytic signals on the BDD than the GC electrode [15–17].

However, Compton and his co-workers have revealed that the electrochemical behavior of the BDD is not always superior to the GC. In their investigations, they have showed that for easily oxidisable compounds like nicotinamide adenine dinucleotide (NADH), the voltammetric responses obtained on the GC and the BDD are similar [18] and oxidation of ascorbic acid takes place at lower potentials on the GC than the BDD [19]. They have also demonstrated that during the electrochemical oxidation of halides [20] and the reduction of chlorine gas [21], different electrodes such as edge plane pyrographite (EPPG), basal plane pyrographite (BPPG) and the GC shows supremacy over the BDD. Moreover, an earlier investigation has clearly indicated that the charge transfer kinetics on the GC and BDD electrodes in aprotic solvents for ferrocene/ferrocenium redox couple are almost similar [22]. The present work is an attempt to explore a close look on these issues.

The anodic oxidation of phenol derivatives in the aqueous medium has served to generate key intermediates in the synthesis of natural products such as neolignans, isodityrosines and triquinanes [23]. Similarly, the electrochemical hydroxylation of methyl substituted aromatic derivatives leads to important precursor for the preparation of vitamin E [24]. With such a background, two compounds namely 2,4-dimethoxyphenol and 1,3,5-trimethylbenzene were taken for this study and their voltammetric characteristics such as anodic peak potential (E_{pa}), anodic peak current (i_{pa}) and multisweep CV responses were explored in aqueous, methanol

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and aqueous-methanolic mixtures at different pHs on the BDD and GC for comparative purpose under identical experimental conditions. Prior to this study, the background potential limits of both the electrodes in all the above media were compared.

2. Experimental

Mesitylene (1,3,5-trimethylbenzene) and 2,6-dimethoxyphenol (Alfa Aesar) were purchased as the highest grade available and used without any further purification. Methanol (HPLC grade), so-

dium acetate (AR), potassium hydroxide (AR) and sulphuric acid were obtained from Sisco Research Chemical, India. Free standing polycrystalline boron-doped diamond electrodes with a mirror finish polish (Diafilm™, mineral acid treated, doping level ca. 10^{20} cm^{-3}, Windsor Scientific Ltd., UK) were obtained as 3 mm diameter discs. The film thickness was approximately 0.5 mm with an average electrical resistivity of 0.75×10^{-3} Ω m. Glassy carbon electrode with the exposed area of 0.03 cm^2 was used as working electrode, in addition to the BDD. A single compartment cell was used with conventional saturated calomel as reference electrode
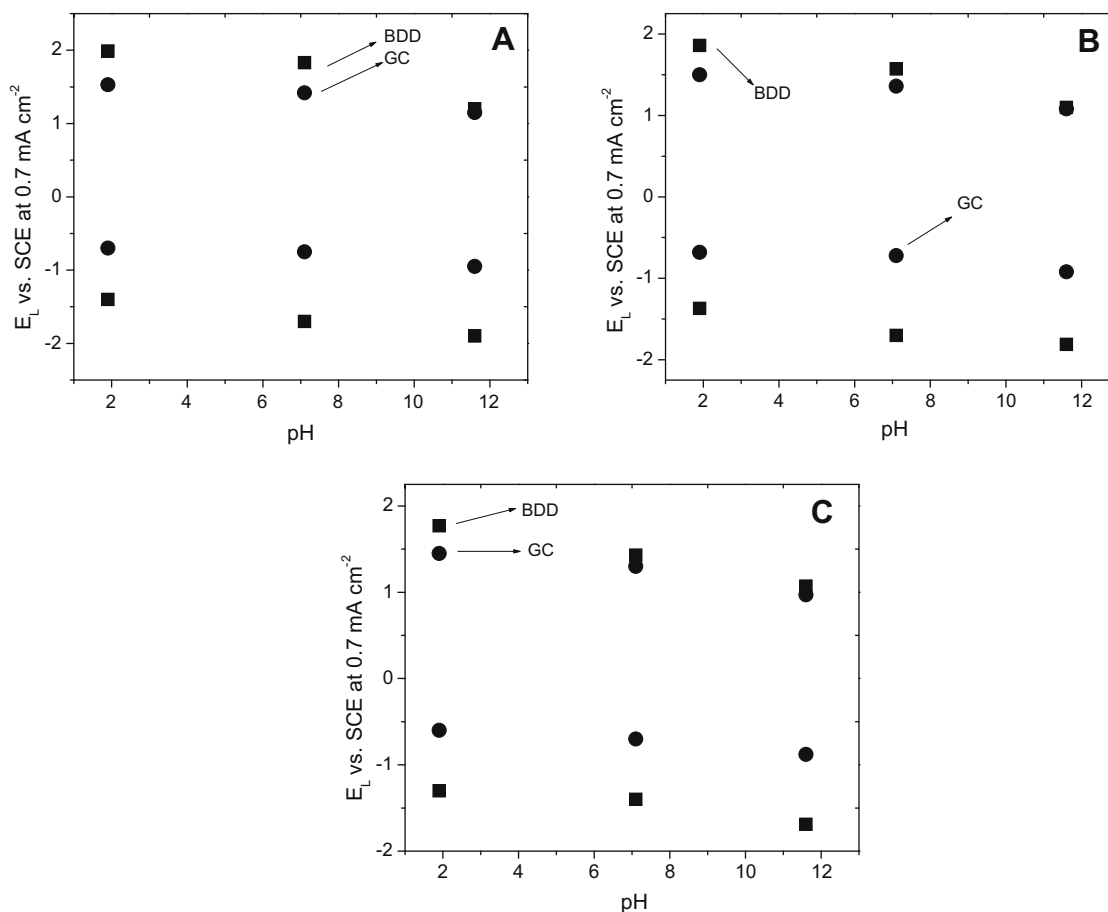

Fig. 1. Plots of limiting potential (E_L, cathodic and anodic) vs. different pHs for the BDD and GC in (A) water, (B) water–methanol and (C) methanol (data obtained from the background voltammograms recorded at a sweep rate of 80 mV s^{-1}).

Table 1
Comparison of the voltammetric parameters of the BDD and GC electrodes in different electrolyte media obtained at a sweep rate 80 mV s^{-1}.

Parameters		pH 1.9			pH 7.1			pH 11.6		
		Water	Water–methanol	Methanol	Water	Water–methanol	Methanol	Water	Water–methanol	Methanol
Background										
E_{la}, anodic	BDD	1.99	1.86	1.77	1.83	1.57	1.43	1.20	1.10	1.07
	GC	1.53	1.50	1.45	1.42	1.36	1.30	1.15	1.08	0.97
E_{lc}, cathodic	BDD	−1.40	−1.37	−1.30	−1.70	−1.70	−1.40	−1.90	−1.81	−1.69
	GC	−0.80	−0.68	−0.60	−0.75	−0.72	−0.70	−0.95	−0.92	−0.88
2,6-Dimethoxyphenol										
E_{pa} (V)	BDD	1.10	1.36	1.58	1.06	1.28	1.38	0.95	1.10	1.21
	GC	0.93	0.98	1.04	0.57	0.55	0.52	0.19	0.15	0.10
I_{pa}	BDD	1.46	1.62	1.84	1.85	1.61	2.67	1.04	0.89	1.00
(mA cm^{-2})	GC	3.78	4.32	5.35	3.43	2.89	5.71	5.27	4.52	6.12
I_{pa}^4/I_{pa}^1	BDD	0.66	0.83	0.99	0.77	0.88	0.99	0.76	0.78	0.81
(Multisweep)	GC	0.60	0.77	0.98	0.56	0.73	0.98	0.60	0.69	0.83

and Pt wire as counter electrode. Voltammograms were recorded in BAS-IM6 system under computer control with Thales USB 3.18 software. All experiments were carried out at 303 ± 1 K.

Triple distilled water was used to prepare all the solutions. The pH of the solution was measured using pH meter (HENNA pHep H1 98107). The solvent-supporting electrolyte solutions were prepared as follows: For acidic (pH 1.9) and neutral (pH of 7.1) solutions, pure H_2SO_4 and sodium acetate were used, respectively. Alkaline solution was made by adding sodium acetate and potassium hydroxide and the pH was adjusted to 11.6. For methanol/water system at different pH levels, water mixed with methanol (in the ratio of 50:50) was employed.

3. Results and discussion

3.1. Background potential window

The accessible anodic (E_{la}) and cathodic (E_{lc}) potential limits obtained from background voltammograms on the BDD and GC in aqueous, methanolic and aqueous-methanolic media at different pH ranges are presented in Fig. 1. It is hereby noted that the potential limit or window is defined as range of potentials observed at a current density 0.7 mA cm^{-2}. For a qualitative discussion, these values are also summarized in Table 1. From Fig. 1, it can be seen that the BDD electrodes in all the solvent systems over the whole pH range have a wider cathodic potential window than the GC

and the potential difference noted between the BDD and GC varies from 0.6 V in aqueous acidic medium to almost 1.0 V in neutral and alkaline media. This demonstrates that this broad window in the cathodic side can be used for the detection of analytes undergoing electro reduction. However, there are only few reports in the literature on the application of the BDD as cathodic sensor material. For example, organic compounds such as 1,3-dinitrobenzene [25], nitrofurazone [26], 2-nitrofluoranthene [27] and trinitrotoluene [28] were detected using the BDD electrode by direct reduction.

On the anodic side, the E_{la} value for the BDD electrode is higher than the GC by almost 0.5 V in aqueous acidic solution (Fig. 1). This difference, however, decreases, upon increasing the methanol content and the pH. In the neutral and alkaline methanolic solutions, the difference in the potential limit between the BDD and GC is only around 0.1 V. Also, it is to be noted that, most of the electroanalytical studies [10] and the electrochemical destruction of organic molecules [1–8] have been carried out in the acidic medium on the BDD electrodes. Unless otherwise, the background limit for the BDD and GC would be almost similar in neutral or alkaline media and in presence of solvents other than water.

3.2. Anodic oxidation of 2,6-dimethoxyphenol

3.2.1. Studies on the anodic peak potential and current

Typical cyclic voltammograms (Fig. 2) obtained for oxidation of 2,6-dimethoxyphenol in aqueous 0.1 M H_2SO_4 (Fig. 2A and C) and
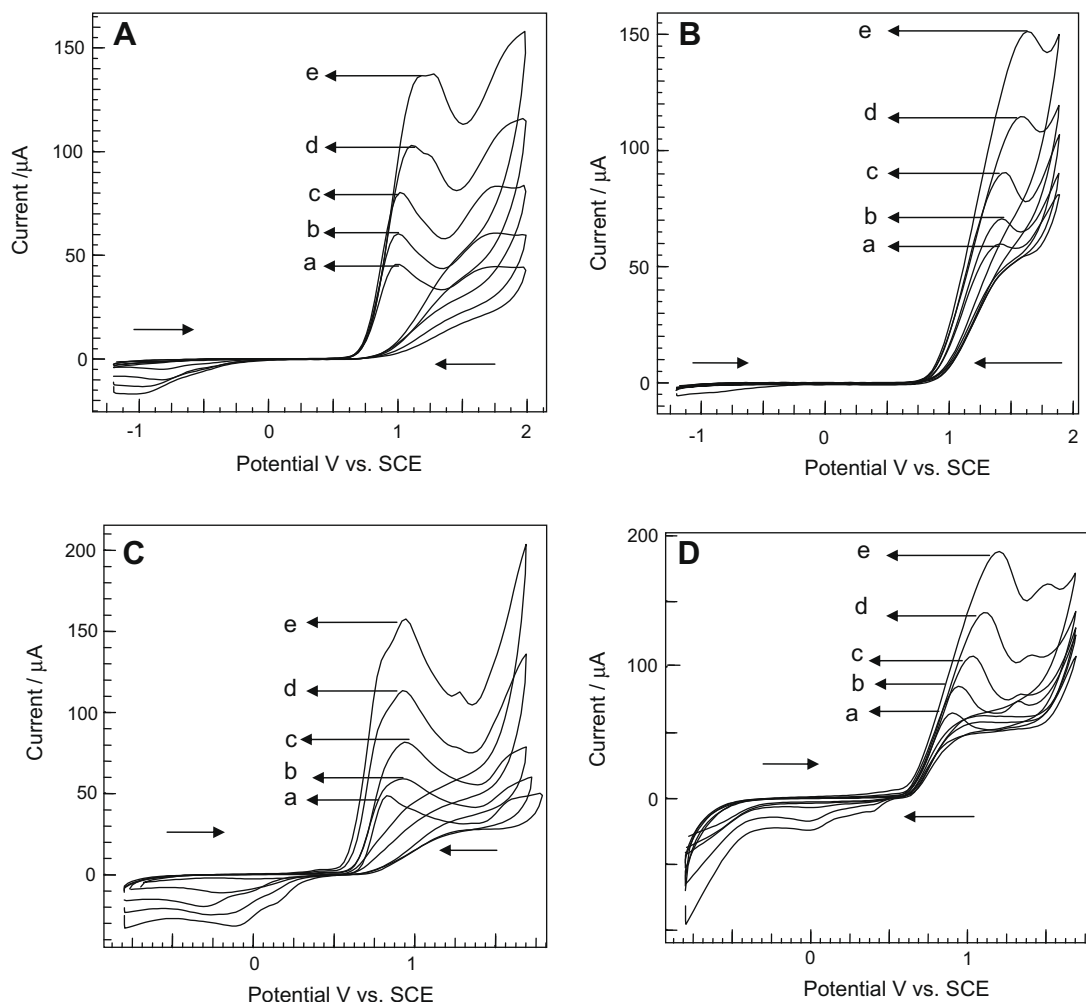

Fig. 2. CVs of 2,6-diemethoxyphenol on (A) and (B) on the BDD and (C) and (D) on the GC electrodes in (A) and (C) 0.1 M H_2SO_4 and (B) and (D) in 0.1 M H_2SO_4/MeOH media at different sweep rates of (a) 10, (b) 20, (c) 40, (d) 80 and (e) 160 mV s^{-1}.

0.1 M H$_2$SO$_4$/MeOH (Fig. 2B and D) on the BDD (Fig. 2A and B) and GC (Fig. 2C and D) respectively at different sweep rates are shown. Both anodic peak potential (E_{pa}) and peak current (i_{pa}) increases with increase in sweep rate. The figures clearly indicate that the anodic peak potential for this compound on the GC in both these media is lower than those obtained on the BDD. Table 1 displays the electrochemical parameters of 2,6-dimethoxyphenol obtained in all the solvent-supporting electrolyte systems employed in this work. From Table 1, it can be seen that 2,6-dimethoxyphenol shows high oxidation overpotential on the BDD when compared to the GC. This is also consistent with recent works done by Compton et al. wherein, they have explored the anodic oxidation of ascorbic acid [19] as well as bromide [20] and reduction of chlorine [21] on the BDD and the GC electrodes. They have also demonstrated that high overpotential is required to oxidise ascorbic acid as well as halides and reduce chlorine at the BDD electrode in comparison to the GC electrode.

Table 1, furthermore indicates that the difference in the E_{pa} values obtained on the BDD and GC increases by increasing the pH and alcohol content. In alkaline methanolic medium, this difference will be as high as 1.10 V. Such difference may lead to a fact that the BDD electrode is not a suitable material for electroanalytical applications in the alkaline medium. A recent report also reveals that an aqueous and methanolic alkaline solutions change the morphology of the BDD surface resulting in surface degradation [29].

The anodic peak current (i_{pa}) values obtained from the CVs for different concentrations of 2,6-dimethoxyphenol on the GC and BDD electrodes in acidic, neutral and alkaline media are compared in Fig. 3 and Table 1. It is interesting to note that in all the three media at different pHs, the i_{pa} values obtained on the GC are considerably higher than the BDD. Table 1 also indicates that for both the electrodes, the i_{pa} value increases with the addition of methanol in acidic and neutral pH solutions; however, decreases for the BDD in alkaline solution (Table 1). Quantitatively, it has been observed that in acidic and neutral media, 2–2.5-fold higher i_{pa} values are obtained on the GC than the BDD and surprisingly, the increase is five fold in the alkaline media. Similar results were also obtained by Compton et al. on the anodic oxidation of bromide [21] and reduction of chlorine [22]. The above results once again reflect the earlier observation on the merits of the GC.

3.2.2. Multisweep cycling and electrode fouling

Under the experimental conditions reported here, no significant difference between the GC and BDD electrodes in terms of reproducibility could be noticed and identical cleaning procedures were found to be sufficient in order to prevent the electrode fouling.

In order to assess the effect of fouling on the electrode surface, a few multisweep cyclic voltammograms (five cycles) were reported. If the intermediates or products get irreversibly adsorbed on the electrode surface, the peak currents in the second and subsequent sweeps would be considerably low due to the formation of passive films on the electrode surface. Typical CVs obtained for the oxidation of 2,6-dimethoxyphenol on the BDD and GC under identical experimental conditions are shown in Figs. 4A and B respectively. From the figures, it is noted that the peak currents in the second
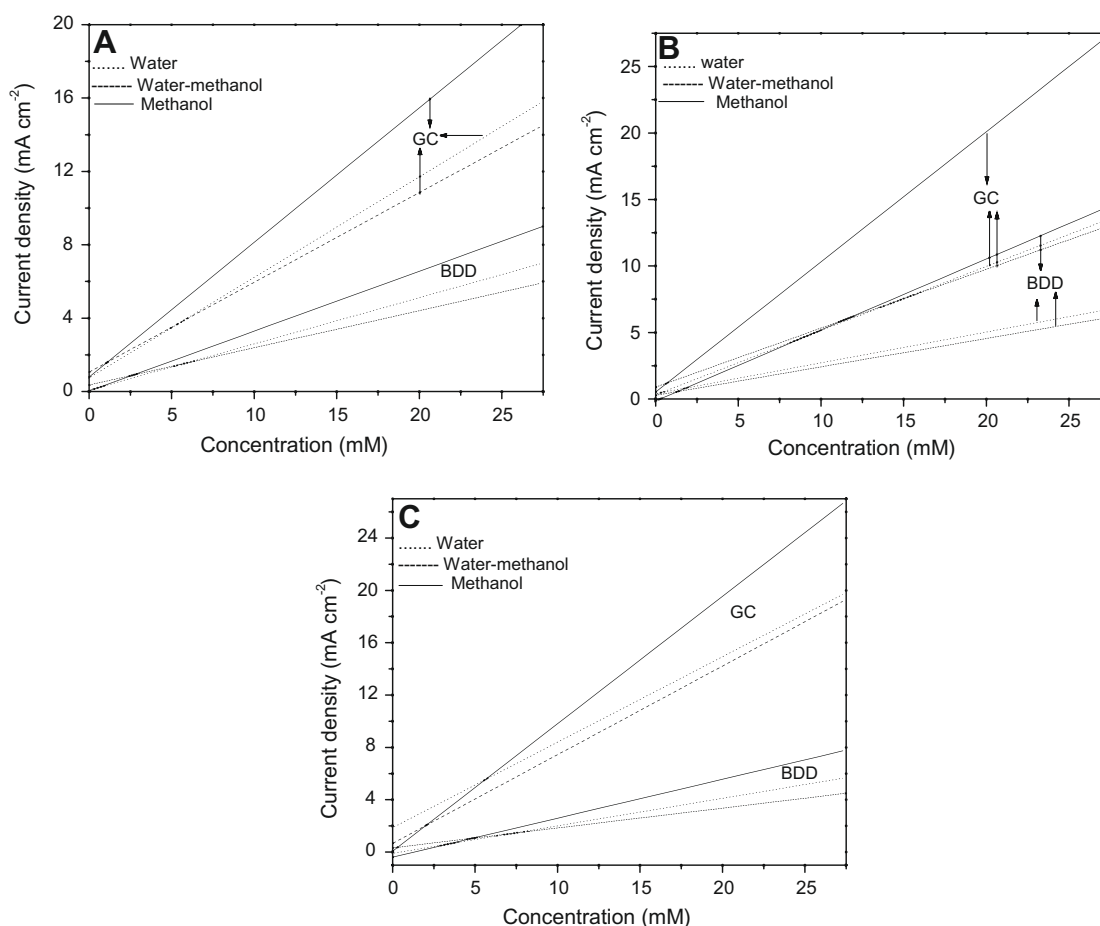

Fig. 3. Plots of anodic peak current obtained from CVs vs. different concentrations of 2,6-dimethoxyphenol on the BDD and GC electrodes in different media at various pHs (A) 1.9, (B) 7.1 and (C) 11.6.

and subsequent sweeps do not decrease significantly on both the electrodes. Quantitatively, i_{pa} value obtained in the fourth cycle (i_{pa}^4) on each electrode is compared with the first anodic peak current value (i_{pa}^1) and the values are presented in Table 1. The i_{pa}^4/i_{pa}^1 ratios for the BDD are always found to be slightly higher than the GC indicating low electrode fouling, if any, on the BDD. In methanolic medium, i_{pa}^4/i_{pa}^1 values are close to unity on the both electrodes indicating devoid of adsorption of organic molecules on these electrodes (Table 1). This reveals the similarity between those electrodes in terms of the contamination of the oxidised species on the electrode surface.

Fig. 4 also indicates another important difference between the BDD and GC in multisweep experiments. The electrooxidation is irreversible on the BDD (Fig. 4A), whereas, it is reversible on the GC (Fig. 4B). A new anodic peak in the second and subsequent sweeps is noticed on the GC (Fig. 4B) and is associated with the formation of quinone/hydroquinone redox couple as reported elsewhere [30]. Since organic compounds generally undergo electrochemical degradation on the BDD easily, such redox couples are not probably formed on this electrode.

3.3. Anodic oxidation of 1,3,5-trimethylbenzene

The voltammetric behavior of 1,3,5-trimethylbenzene was also investigated on the BDD and GC surfaces under identical conditions. No distinct oxidation peak was observed for this compound on the GC electrode in all the above media. Typical CVs obtained on the BDD electrode for the electrooxidation of 1,3,5-trimethylben-

zene at different sweep rates and concentrations are shown in Figs. 5A and B respectively. From the figure it is noted that at a slow sweep rate, a broad oxidation wave is observed on the BDD near the background oxidation potential region in the acidic medium (Fig. 5A). The peak current increases with increase in sweep rates (Fig. 5A) and concentrations (Fig. 5B). However, the peaks becomes broad with increase in concentrations of 1,3,5-trimethylbenzene and at a high concentration (10 mM) of 1,3,5-trimethylbenzene, the peak almost disappears (Fig. 5B). It has been also observed that the oxidation peak current of the 1,3,5-trimethylbenzene obtained after the background correction is found to be low and also do not increase consistently by increasing its concentration.

Further, we had explored the effect of addition of methanol on the oxidation of 1,3,5-trimethylbenzene on the BDD in acidic medium also. With subsequent addition of methanol, the broad wave disappeared. Even in aqueous neutral and alkaline media, no anodic peak appeared on the BDD electrode.

From the above voltammograms, it is clearly understandable that oxidation of 1,3,5-trimethylbenzene takes place near the potential region of gas evolution region in the acidic medium only on the BDD, whereas in the neutral as well as alkaline solutions, the electrooxidation reaction takes place along with the oxygen evolution, resulting in the absence of any anodic peak both on the BDD and GC. From an analytical point of view, it appears that
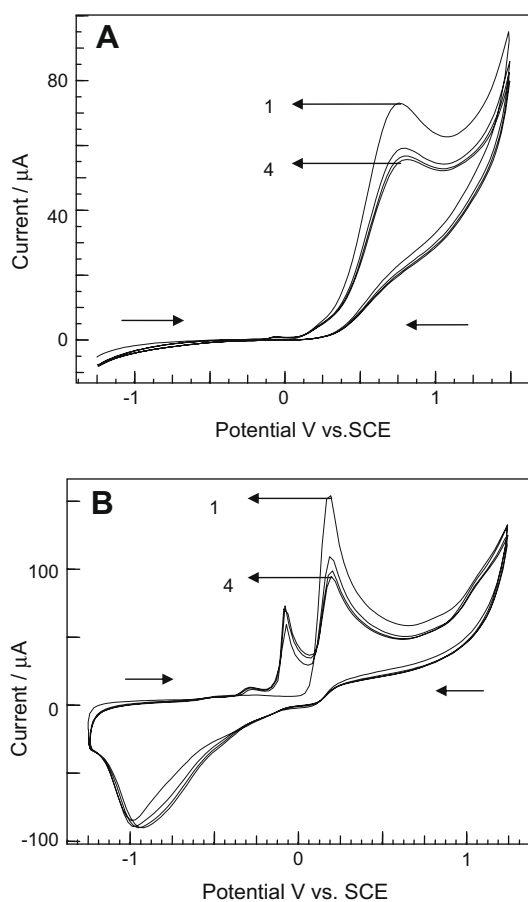

Fig. 4. Effect of multisweeps (five cycles, 80 mV s^{-1}) on the oxidation of 2,6-dimethoxyphenol on (A) BDD and (B) GC in 0.1 M NaOAc/KOH aqueous solution (pH 11.6).
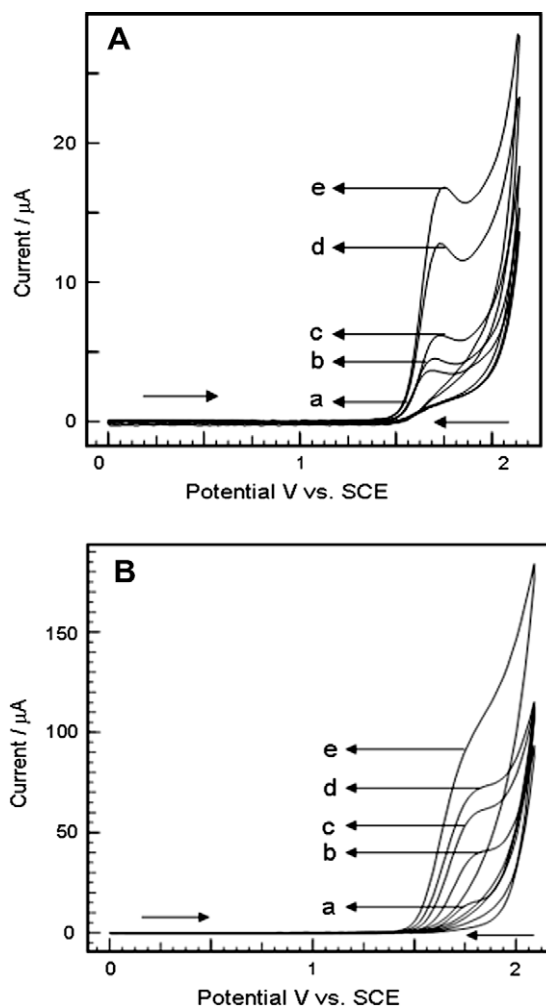

Fig. 5. CVs of 1,3,5-trimethylbenzene (6 mM) on the BDD electrode in 0.1 M H$_2$SO$_4$ solution taken at (A) different sweep rates (a) 10, (b) 20, (c) 40, (d) 80 and (e) 160 mV s^{-1} and (B) various concentrations (a) 2, (b) 4, (c) 6, (d) 8 and (e) 10 mM at a sweep rate of 80 mV s^{-1}.

even in the acidic medium, such a low oxidation peak current observed for 1,3,5-trimethylbenzene on the BDD may not be very useful either for its detection using voltammetric/amperometric investigations or for the bulk electrolysis and any electro-synthetic reactions involving the above compound may lead to complete incineration. As an alternative to study the electrooxidation process of such organic compounds with relatively high oxidation potential, EPPG may be the electrode of choice, as suggested by Compton et al. [31,32].

We have carried out only a preliminary work related to this comparative study and further in-depth electrochemical investigations involving different analytes in various solvent-supporting electrolyte media will be explored in our laboratory for the evaluation of suitable electrode material.

4. Conclusions

The above work has revealed that the BDD electrode possesses wider cathodic potential window and lower background current in all the media than the GC. In the anodic side, the window was wide only in aqueous acidic medium and the background limits for both the electrodes was similar in both neutral and alkaline media containing solvents other than water. Even in the acidic medium, the anodic oxidation of 2,6-dimethoxyphenol took place at less potential on the GC when compared to the BDD and the oxidation peak current was also higher on the former electrode. Further, the adsorption effect of this compound was almost negligible on the surface of both the electrodes indicating the requirement of similar precautions and pre-treatment procedures in order to achieve high reproducibility. It may be concluded that for the oxidation of organic compounds with high over potential, GC is not the electrode of choice at all in any media and the BDD electrode may be substituted at least in the acidic medium. However, its applicability for such electrooxidation process, even in this medium, is still under question.

Acknowledgements

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