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Electrochemistry with boron-doped diamond electrodes

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ABSTRACT

In recent years, conductive diamond electrodes for electrochemical applications have been a major focus of research and development. It occupies a special place as an electrode material with interesting applications in electroanalysis. This review article summarizes some of the recent work on the use of boron-doped diamond electrodes for electrochemical applications.

KEYWORDS

Boron-doped diamond;
Electroanalysis;
Voltammetry;
Stripping voltammetry;
Wastewater treatment.

INTRODUCTION

Diamond is best known as the hardest substance. It is also the best known thermal conductor and has very high electron carrier mobility. It also exhibits exceptional optical (high refractive index, wide band gap), tribological (low friction co-efficient) and electrochemical properties (high overpotential for both oxygen and hydrogen gas evolution). TABLE 1 illustrates some basic properties of diamond. Synthetic high purity diamond or natural diamond is an electrical insulator with a breakdown voltage upto 10^9 V m^{-1}. Hence, it can not be used as an electrode material. However, if it is doped with boron (B) atom, boron-doped diamond (BDD) will become conductive and it behaves as a new type of electrode material with interesting applications in electroanalysis. BDD electrodes are made of polycrystalline diamond formed by Chemical Vapour Deposition (CVD) in a high temperature process. In the tetrahedral diamond lattice, each carbon atom is covalently bonded (sp^3) to its neighbours forming an extremely robust crystalline structure. Some carbon atoms in the lattice are substituted with boron to provide electrical conductivity. Boron acts as an electron acceptor due to its electron deficiency in its outer shell.

TABLE 1 : Some basic properties of diamond

Property	Single crystal Diamond
Density (g cm^{-3})	3.52
Melting point (K)	4027
Dielectric constant	5.7
Refractive index	2.42 at 546 nm
Thermal conductivity	20 W cm^{-1} K^{-1} at 300 K
Vickers hardness (GPa)	57-104
Electrical Resistivity (Ω cm)	10^{16}
Electronic band gap (eV)	5.5

Boron concentrations (10^{18} – 10^{21} atom cm^{-3}) produce a film resistance of 10^4-10^2 Ω, respectively. The electrochemical studies of diamond thin films started in the mid 80's and interest in this area of research rapidly increased. The first papers were devoted to the fabrication of thin films of diamond[1]. These studies showed that conducting diamond electrodes could be grown in the form of thin films by energy-assisted (plasma or hot-filament) chemical vapour deposition (CVD) on several substrates like silicon (Si), titanium (Ti), niobium (Nb), tantalum (Ta), molybdenum (Mo), tungsten (W), glassy carbon (GC) etc. However, there are some disadvantages of this fabrication technique. A Si substrate is very brittle, Nb,Ta,W are very expensive and the diamond film deposited on Ti is unstable during long term electroanalysis. In order to make diamond films conducting, they are doped with different concentrations of boron atoms and other dopants such as hydrogen, nitrogen and phosphorous.

At extremely low boron-doping level, the diamond electrode is optically transparent over a wide-range of wavelengths. Thus, thin diamond film had been employed as electrode material for in-situ spectroelectrochemical studies[2,3]. For moderate B-doping of 10^8 B atom per cm^3, the electrode behaves as semiconductor, whereas, it becomes semimetal for high doping of $10^{20} \sim 10^{21}$ B atoms per cm^3. High quality BDD electrode exhibits several important properties compared to other type of electrode materials including carbon-based and metallic electrodes. These are

i) An extremely wide potential window in both aqueous and non-aqueous electrolytic media. In case of high quality BDD electrode, hydrogen evolution starts at about -1.25 V vs SHE (saturated hydrogen electrode) and oxygen evolution begins at + 2.3 V vs SHE.
ii) It exhibits very low double-layer capacitance and background current. The double-layer capacitance is one order of magnitude lower than that of glassy carbon electrode.
iii) Corrosion stability in very aggressive media.
iv) High mechanical robustness.
v) Excellent chemical inertness with low tendency of surface oxidation and fouling. Hence, the surface of BDD electrode with low adsorption properties has strong tendency to resist deactivation.
vi) Biocompatible.

This review summarizes some of the recent developments and novel applications of BDD electrodes.

ELECTROCHEMISTRY OF BDD ELECTRODES

BDD electrodes have been used increasingly in electrochemical studies due to their low back-ground current, high current density electrolysis (1-10 A cm^{-2}), a wide potential window, anti-adsorption behaviour and high overpotential for both hydrogen and oxygen evolution. Thin-film diamond electrodes often possess some sp^2 carbon (C) impurities, which can be deactivated by anodic oxidation in aqueous electrolytes. In cyclic voltammograms, it will exhibit an anodic current peak, starting from oxygen evolution. This anodic current peak rapidly diminishes with repeated scan. Higher is the sp^2 C content, lower is the potential window between hydrogen and oxygen evolution in aqueous electrolytes. These sp^2 C active sites, which are present at the grain boundaries, behave electrochemically like edge planes of highly oriented pyrolytic graphite in nitric acid. These sp^2 carbon active sites can be activated by anodic polarization at 1.7-1.8 V vs Ag/AgCl in 1M HNO_3.

BDD electrodes are electrically heterogeneous with conductivity and electron transfer rates varying across the surface. This behaviour can also be confirmed by microscopic characterization and redox activity of both H-terminated[4] and O-terminated[5] BDD electrodes.

Cyclic voltammetry is often employed to study the electrochemical response of BDD electrode using various redox systems such as $Fe(CN)_6^{3-/4-}$,$Ru(NH_3)_6^{3+/2+}$, $IrCl_3^{3-/4-}$, $IrCl_6^{3+/2+}$, BQ/HQ and Fe^{3+}/Fe^{2+}. A wide range of data obtained from voltammetric studies performed on BDD electrodes had been published[6]. Some standard redox systems had been proposed to provide data for high-quality BDD characteristics.

There are two types of reactions in heterogeneous electron transfer. The first type involves electrode reactions that proceed by simple mass transfer of redox molecules to the electrode|electrolyte interface and the electrode serves as a source or sink for electrons. The electrode kinetics are relatively insensitive to surface chemistry and microstructure, but very sensitive to the electronic density of states close to the formal potential. This is called outer-sphere redox reaction.

The second type involves electrode reactions that proceed via some specific interaction of the redox molecules with the electrode surface. In this case, electrode kinetics are sensitive to surface chemistry and microstructure, as well as electronic density of states near the formal potential. This is called inner-sphere redox reaction.

The outer-sphere reactions include $Ru(NH_3)_6{}^{3+/2+}$, ferrocene $^{+/-}$, anthracene $^{+/-}$, and $IrCl_3{}^{3-/4-}$. Most conducting diamond electrodes have lower density of electronic states compared to the graphitic carbon and this may be the reason for the slower kinetics of outer-sphere systems on BDD electrode.

Although, the $Ru(NH_3)_6{}^{3+/2+}$ redox couple exhibits its classical voltammetric waves on BDD electrodes, similar to those obtained by glassy carbon electrode, the rate constant on BDD electrode is much slower (0.012-0.017 cm s^{-1}) compared to GC electrode (0.51 cm s^{-1}). The voltammetric responses for $Fe(CN)_6{}^{3-/4-}$ and $Ru(NH_3)_6{}^{3+/2+}$ on BDD electrodes reveal the absence of double-layer effects, which are commonly observed on GC and other sp^2 carbon based electrodes. The heterogeneous rate constant of 0.01/0.02 cm s^{-1} are typical for both conducting microcrystalline and nanocrystalline films without extensive pre-treatment. Cyclic voltammograms of a platinum and H-terminated BDD electrode with redox couple $Fe(CN)_6{}^{3-/4-}$ are comparable, although, Pt is more reversible[7]. The doping level and pre-treatment of the BDD electrode play an important role on the kinetics of heterogeneous charge transfer reactions. BDD film electrodes exhibit a 1.5~ 2.5 times wider potential window (~ 5-7.5 V) in non-aqueous electrolytic media than the aqueous electrolyte.

ANALYTICALAPPLICATIONS OF BDD ELECTRODES

The use of mercury has been banned in most of the developed countries of world. Thus, mercury based electrodes are not used for electroanalytical applications. Carbon based materials such as graphite and GC electrodes provide a large overpotential for hydrogen evolution. But such electrodes undergo surface oxidation and biofouling processes. These carbon based electrodes will react with oxygen and water to form oxygen-containing functional groups such as phenol, lactones, carboxyls, ethers and carboxylates on the electrode surface. Therefore, they might require considerable surface cleaning and conditioning and are less suitable for electroanalytical applications. In contrast, no oxide formation and reduction reactions between oxygen and hydrogen evolution occur on BDD surfaces.

In (bio)sensing applications, both the pristine and modified diamond electrodes can be employed, depending on the specific analyte. Their low capacitive current, large potential window and high stability, sensitivity and a low detection limit can be utilized for electroanalysis. Several electroanalytical techniques such as amperometric detection, anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), abrasive stripping voltammetry (AbSV) and square wave voltammetry (SwV) have been employed with BDD electrodes. The target analyte can be an organic compound or an inorganic species including metal ions.

In AbSV, the polycrystalline BDD electrode is scratched across the surface of an analyte and small quantities of analyte sample transferred during this process are then detected by stripping voltammetry after immersing the electrode in a suitable electrolytic medium. However, the unreliable electrical contact between the sample and BDD surface can cause problem. Manivannan *et al.*[8] first reported the experimental use of AbSV technique in lead (Pb), iron (Fe) and alloy analysis. Recently, a refined abrasion process was introduced with silver (Ag) and tin (Sn) samples[9].

Electrochemical stripping analysis with BDD electrodes might be a powerful tool for detection of trace amount of hazardous metals such as Pb, Cd, Hg, As, Th, Se etc. in ppb or ppt limits. Various anions, metals and organic compounds have been analyzed by BDD electrodes (See TABLE 2 and TABLE 3).

TABLE 2 : Analysis of inorganic ions and metal ions

Target Analyte	Electrode Material	Limit of detection
Azide ion	H-terminated BDD	8 nM
Hydrazine	Pd nanoparticles on BDD	2.5 μM
H_2O_2	Pt modified BDD	30 nM
Nitrate	Cu nanoparticles on BDD	1.5 μM in mineral water
Nitrite	Cu nanoparticles on BDD	7 nM
As(III)	Pt nanoparticles modified BDD	0.5 ppb

TABLE 3 : Analysis of organic compounds

Target Analyte	Limit of detection
Adenosine	10 nM
Ascorbic acid	12 nM
Caffine	1-400 μM
Chlorophenols	1-250 μM
p-cresol	1-200 μM
Dopamine	50 nM
Glucose	670 nM
Sulfa drugs	50 nM
Tetracycline	10 nM
Xanthine	1-100 μM

Amperometric detection can be performed with flow injection analysis (FIA) HPLC and capillary electrophoresis (CE) including the CE chip.

One considerable advantage of BDD electrodes over other types of electrodes is the chemical stability at very positive potentials along with a low background current and high overpotential for oxygen evolution reaction. These characteristics introduce new opportunities for anodic electrochemical detections. On conventional electrode materials such as metal or glassy carbon, oxidation of phenols is blocked by large background current and followed by formation of poly(phenoxy) type deposits. This process complicates analytical detection. Pollutants such as chlorophenols had been detected at BDD electrodes in a flow-through electrochemical cell[10]. The oxidation of 4-chlorophenol, 2-chlorophenol, 2,4-dichlorophenol, phenol and 4-chloro-3-methyl phenol have been observed at + 1.5 V vs SCE in acidic aqueous solution at BDD electrode. In a flow-cell configuration, detection upto 20 μM had been carried out. The detection of chlorophenols at BDD electrodes in the presence of ultrasound had also been reported[11].

Sonoelectrochemistry introduces several improvements in electroanalysis such as better signal to noise ratio and absence of laborious sample pre-treatment processes. Depending on the mechanical hardness of the electrode material, considerable damage to the electrode surface takes place within a short period of time in the presence of power ultrasound . BDD electrodes under power ultrasound have been demonstrated to show no signs of cavitation or mechanical damage due to the robust mechanical hardness of diamond surface[11]. The detection of 4-chlorophenol by oxidation at BDD electrode in the presence of 20 kHz ultrasound had been reported to be possible with a lower detection limit of about 1 μM concentrations and a linear range of 1-300 μM in aqueous media[11]. Saterlay *et al.*[11] reported the successful development of an aqueous 4-chlorophenol voltammetric sensor. The use of power ultrasound during the electrooxidation of 4-chlorophenol at BDD electrode had also been shown to be beneficial in the electrochemical degradation of this pollutant, which need to be constantly monitored in the aquatic environment, potentially offering further waste-water clean-up applications. Similar to phenols, organic pollutants such as dyes tend to form passivating layers on electrode surfaces. A study on the detection and bleaching of reactive dye Procion Blue revealed that the formation of the passivating layer occurs gradually. At low dye concentrations, well-defined quasi-steady state voltammograms are observed in the presence of ultrasound and well-defined analytical signals were obtained over a concentration range upto approximately 50 μM[12].

The direct oxidation of L-cysteine was compared on GC and BDD electrodes[13]. Slower kinetics due to the desorption of L-cysteine on GC electrode exhibits much poorer voltammetric response. In contrast, BDD electrode was used to detect this amino acid directly down to μM concentration range.

The voltammetric behaviour and detection of sulfadiazine drug and of NADH (nicotinamid adenine dinucleotide) were reported at BDD thin film and microelectrodes[14]. Similarly, electrochemical analysis of different nucleic acids had also been reported on BDD electrodes[15]. tRNA, single and double stranded DNA and 2'- deoxyguanosine 5'-monophosphate (dGMP) were well studied and well-defined voltammetric peaks were observed in all the cases, which had been directly assigned to the electrooxidation of deoxyguanosine monophosphate.

Other nitrogen containing organic compounds (dopamine, indole, aminochrome) had been studied on polycrystalline BDD electrodes[16]. The oxidation of Xanthine derivatives and caffeine were reported at the BDD electrodes[17]. Antidepressant drugs such as imipramine, desipramine, clomipramine, amitriptyline and doxepin were readily oxidized at both BDD and GC electrodes[18]. However, background current were reduced and detection procedure was more reproducible at the BDD electrode compared to GC electrode.

Both CSV and ASV offer powerful tools for the detection of trace levels of metals and impurities[19] and these techniques are based on the amplification of the analytical response by a pre-accumulation/pre-concentration step. Stripping voltammetry is a powerful electroanalytical technique for the detection of trace amount of metals in the range of ppb (parts per billion). Its high sensitivity is attributed to the pre-concentration step, during which the target metals are accumulated/deposited on to the working electrode. Early works were focused mainly on metal deposition and stripping processes at BDD electrodes. The detection of trace levels of Pb at BDD electrode by ASV was reported by Fujishima *et al.*[20]. The electrochemical detection of ionic mercury in the concentration range from 10^{-10} to 10^{-5} M at BDD electrodes were reported by Manivannan *et al.*[21]. The extremely low back ground current for BDD electrodes provides a strong advantage in trace metal detection.

The use of thermal activation in electroanalysis offers various benefits[22]. The use of focused microwave activation in electrochemistry was first reported by Compton *et al.*[23] and has since been investigated for various interfacial processes such as adsorption[24], metal deposition[25], and electron transfer reactions[26]. It has been shown that at metal electrodes self-focusing of the microwave radiation occurs[27] and a very high power density is available directly at the tip of the electrode immersed in electrolytic solution. Most electrochemical studies with microwave radiation have been carried out with metal electrodes. In one of the preliminary report, the microwave activation of electrochemical processes for the deposition and stripping of PbO_2 at carbon and BDD electrodes had been reported[28]. The microwave-enhanced anodic stripping detection of Pb in a river sediment had been proposed as a novel procedure employing a BDD electrode[25].

BDD ELECTRODE FOR WASTE WATER TREATMENT

Electrochemistry provides an attractive alternative to traditional methods for waste water treatment[29]. Several carbon-based electrodes have been used for waste water treatment, but some of them demonstrated a rapid loss of activity due to the fouling of the electrode surface[30]. Anode materials like IrO_2 gave selective oxidation, while PbO_2 released toxic ions and SnO_2 showed a limited service life.

On the other hand, BDD electrode has proved to be excellent material for waste water treatment and water disinfection due to its high anodic stability and wider potential window. The oxidation of organic compounds at the BDD electrode can follow two mechanisms depending on the applied potential. The first one is the direct electron transfer in the potential region before oxygen evolution (water stability). The second one is the indirect oxidation via electrogenerated hydroxyl radicals ($OH^{\cdot}$), in the region of oxygen evolution (water decomposition).

On the basis of different experimental results, Comninellis[31-33] proposed a mechanism for the oxidation of organic compounds with the evolution of oxygen concurrently. This assumes that both organic oxidation and oxygen evolution can take place on a BDD electrode via the formation of $OH^{\cdot}$ radical as the intermediate through the electrolysis of water.

$$\mathbf{BDD + H_2O \rightarrow BDD\ (OH^{\cdot}) + H^{+} + e^{-}} \qquad (1)$$

$$\mathbf{BDD\ (OH^{\cdot}) + R \rightarrow BDD + m\ CO_2 + n\ H_2O} \qquad (2)$$

$$\mathbf{BDD\ (OH^{\cdot}) \rightarrow BDD + \tfrac{1}{2}\ O_2 + H^{+} + e^{-}} \qquad (3)$$

Reaction (2) is in competition with the side reaction (3) of hydroxyl radical discharging into O_2.

A large number of organic pollutants are completely mineralized by the reaction of electrogenerated hydroxyl radical during the electrolysis at BDD electrodes at high applied potential[34-36].

SUMMARY

Diamond electrodes and in particular highly B-doped diamond electrodes are highly beneficial in many applications in electroanalysis[37,38], waste water treatment[39]. It has been shown that BDD is much better electrode material compared to GC and other traditional electrode materials. However, despite the several benefits of BDD electrodes, they have not found wide industrial applications, mainly due to their high cost and the difficulties to find a suitable substrate for the deposition of thin diamond films.

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