

Preliminary Investigation on the Redox Behavior of Dopamine/Aminochrome at the Boron-Doped Diamond Electrode by Cyclic Voltammetry

Rajeshuni Ramesham*

Space Power Institute, 231 Leach Center, Auburn University, Auburn, AL 36849-5320, U.S.A.

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Chemical vapor deposition (CVD) of highly doped polycrystalline diamond thin films were grown by a microwave plasma process using a methane and hydrogen gas mixture at a pressure of 34 – 35 Torr over a mechanically damaged and cleaned molybdenum substrate. Boron doping of diamond was achieved *in situ* using a solid disc source of B₂O₃. The doped diamond was evaluated in a 0.5 M NaCl supporting electrolyte solution for a background current response, by cyclic voltammetry. We observed a negligible background current over a wide potential range for boron-doped diamond. Decomposition of water occurs electrochemically and generates oxygen at high positive (anodic) polarization and hydrogen at high negative (cathodic) polarization. We have studied the redox kinetic behavior of dopamine/aminochrome at the diamond electrode in a solution of 0.5 M NaCl. All the experimental measurements were corrected for uncompensated current times resistance (IR) and background current. The background current response was also corrected for uncompensated IR.

1. Introduction

Diamond is a possible candidate material for numerous applications due to its unusual combination of chemical and physical properties.⁽¹⁾ Several potential applications can be anticipated for diamond in bioelectroanalytical detection of neurotransmitters, protective corrosion-resistant coatings, electroanalytical chemistry, applied electrochemistry, elec-

*Present address: Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA - 91109, U.S.A.

tronics, wear-resistant coatings (cutting tools), field emission, secondary electron emission, optical coatings, dielectric material, high-temperature devices and optics, based on its properties. Our goal is to demonstrate diamond applicability for the detection of neurotransmitters by electroanalytical techniques. Cyclic voltammetry can be used to explore the nature of easily oxidized catecholamine and indoleamine neurotransmitters, metabolites, and other related compounds. The voltammetric method can specifically be used to study dopamine (3-hydroxytyramine hydrochloride) and its metabolites (dihydroxyphenyl acetic acid, DOPAC and homovanillic acid, HVA), and serotonin and its metabolites (norepinephrine and ascorbic acid). The electrochemical oxidation of dopamine occurs in a reaction sequence in which the electron transfer step generates a product that undergoes a chemical reaction to form a new product that is electroactive at the potential of the first reaction. The reaction mechanism may be referred to as ECE where E is the heterogeneous electron transfer step and C is for the homogenous chemical step.⁽²⁾ Figure 1 shows the mechanism of electrochemical oxidation of dopamine to dopamine o-quinone and indole to aminochrome.

Glassy carbon, highly oriented pyrolytic graphite (HOPG), platinum (Pt), the dropping mercury electrodes (DME, Hg), carbon paste, graphite and gold (Au) are the general materials of interest for electroanalysis, since they each have a large usable potential range in acidic solutions.⁽³⁾ Glassy carbon and other solid electrodes will normally become deactivated when they are exposed to electrolyte solutions for a long time. Glassy carbon may be reactivated by several approaches, such as mechanical and electrochemical polishing, plasma, heat or annealing treatments. Fagan *et al.*⁽⁴⁾ described the activation of glassy carbon electrodes using vacuum heat treatments, and the references therein describe other activation procedures. Since HOPG is very soft, Pt and Au very expensive, and Hg considered to be toxic, a search for alternative robust electrode materials for electroanalyti-

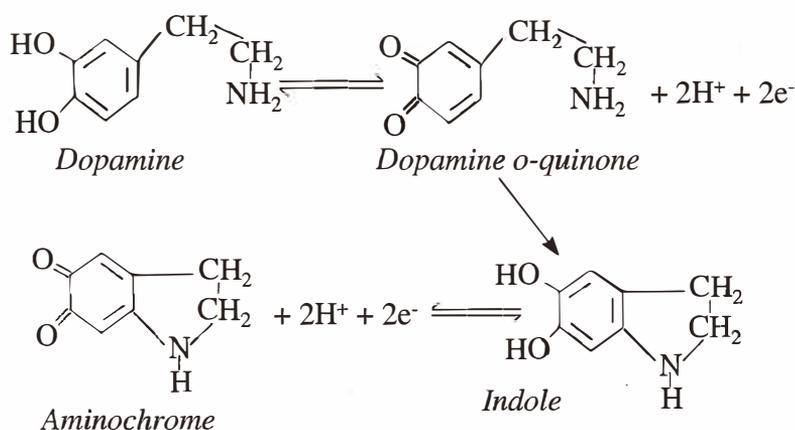


Fig. 1. Mechanism for the electrochemical oxidation of dopamine to dopamine o-quinone and indole to aminochrome.

cal applications is required.

McCreery and Cline⁽⁵⁾ provided an excellent overview of carbon electrodes for electroanalytical applications. The voltammetry of neurotransmitters and their metabolites with various electrode materials have been extensively studied in the past.⁽⁶⁻¹⁵⁾ There have been some reports on the characterization of diamond films by electrochemical techniques. Ramesham *et al.*⁽¹⁶⁾ demonstrated the growth of polycrystalline CVD diamond over glassy carbon and graphite electrode materials for use in applied electrochemistry and electro- and bioelectroanalytical chemistry. Alehashem *et al.*⁽¹⁷⁾ and Strojek *et al.*⁽¹⁸⁾ reported the cyclic voltammetric behavior of dopamine neurotransmitter using boron-doped diamond films. Ramesham and Rose^(19,20) reported the electrochemical behavior of doped diamond in 0.5 M NaCl solution using electrochemical AC impedance spectroscopy and DC polarization techniques; they also showed that the diamond electrode material is stable over a wide potential range for the decomposition of H₂O to produce hydrogen and oxygen during cathodic and anodic polarization, respectively, in various electrolytes.⁽²¹⁾ In this paper we report the voltammetric behavior of dopamine to aminochrome in a 0.5 M NaCl solution at a boron-doped diamond electrode since this material has a very high usable potential range due to its insignificant background current and low double-layer capacitance compared to other conventional materials.

2. Experimental Details

Surface damaging is a necessary process to nucleate CVD diamond on nondiamond substrates. Ultrasonic agitation of the molybdenum substrates is performed in methanol containing synthetic diamond particles with typical sizes of 60–90 μm for 10–60 min and washed with tap water, acetone, methanol and deionized water.⁽²²⁻²⁴⁾

A microwave plasma (2.45 GHz)-assisted CVD system (ASTeX) has been used to grow polycrystalline diamond films. A schematic of the diamond deposition system has been described previously.⁽²²⁾ The molybdenum substrate was placed at the center of the stage that was then loaded into the quartz bell jar reactor which was evacuated to a base pressure of 10^{-4} Torr. A plasma was obtained by adjusting the pressure in the chamber, the hydrogen flow rate, microwave power and waveguide tuning. The substrate was heated *in situ* by the microwave plasma to attain the desired substrate temperature ($925 \pm 25^\circ\text{C}$) before initiating the diamond growth. We did not use an extra heater to raise the temperature of the substrate. Ultrahigh-purity-grade hydrogen and research-grade methane were used in our experiments to deposit the diamond films. The temperature was remotely monitored by an optical pyrometer. Diamond deposition was initiated by injecting methane into the system when the substrate reached the desired temperature. The deposition rate under the typical conditions was normally 0.5–1 $\mu\text{m/h}$.⁽²⁴⁾ A continuous film of diamond was usually obtained after 10 to 20 h of growth.

Boron doping of diamond films was achieved using a solid disk source consisting of B₂O₃ and other oxides. The solid disk source of boron has been used as a base of the molybdenum substrate during growth of *in situ* doped diamond at a substrate temperature of 950°C. The size (30 mm \times 30 mm) of the boron source disk is greater than that of the

substrate (21 mm × 21 mm). The doping source disk can be exposed to the hydrogen and methane microwave plasma at 950°C and will result in *in situ* diamond doping.⁽²⁴⁾ We measured the electrical resistivity of a boron-doped diamond sample deposited under identical conditions and it was found to be in the range of 1–10 Ω·cm. The dopant concentration of boron in diamond deposited under similar conditions was on the order of 1000 ppm.

All solutions were prepared using reagent-grade chemicals in deionized water. Voltammetric studies were performed using various concentrations (0.01, 0.1, 1 and 5 mM) of dopamine in 0.5 M NaCl solution. Cyclic voltammograms were obtained at various scan rates of 10 mV/s to 1000 mV/s. The apparent exposed area of the boron-doped diamond is 0.71 cm². The effective area of the electrode surface that is corrected for surface roughness is 0.82 cm².⁽²⁵⁾ A reference electrode of Ag/AgCl (0.5 M NaCl) was used in this study. A platinum counterelectrode was used in all the electrochemical polarization measurements which were conducted at room temperature, ~25°C. The solution was not purged with nitrogen prior to any electrochemical measurements. A simple single-compartment, three-electrode electrochemical cell was used in this study. A potentiostat (EG&G Model 273) was used in our experiments to perform the cyclic voltammetry. All experimental data was corrected for uncompensated IR unless otherwise stated. The voltammetry response was obtained using the diamond electrode in 0.5 M NaCl solution containing dopamine, from which the background current response was subtracted. The solution was not stirred during the cyclic voltammetry experiments, and the area of the electrode is fixed in all of the experiments reported in this paper.

3. Results and Discussion

The diamond films had a well-faceted morphology, as observed by scanning electron microscopy. Films grown using a microwave plasma CVD reactor under similar experimental conditions have been previously analyzed by Raman spectroscopy.^(16,22-24) As-deposited CVD diamond films have a roughness factor that varies from 0.1 to 1 μm, as determined by profilometry.⁽²²⁾

Figure 2 shows the background current response for a highly conducting boron-doped CVD diamond electrode immersed in a supporting electrolyte of 0.5 M NaCl at various scan rates of 10, 25, 50, 100, 500 and 1000 mV/s, determined by cyclic voltammetry. From Fig. 2 it is clear that the doped-diamond electrode is relatively stable over a wide potential range. Here, insignificant water decomposition has occurred, and there are no voltammetric features associated with any electrochemical process. Therefore, the doped diamond can be useful in bioelectroanalytical chemistry. The wide potential range observed could be partly due to the chemical inertness of diamond. The maximum current observed within this potential range (–650 to +1200 mV) was approximately 25 μA (apparent electrode area: 0.71 cm²) at a scan rate of 100 mV/s. Therefore, it is possible to study the kinetics of any redox process that occurs at the solid electrode/solution interface within this potential range. We did not observe any change to the surface of the diamond electrode after the performed experiment in Fig. 2, using scanning electron microscopy. We predict that the

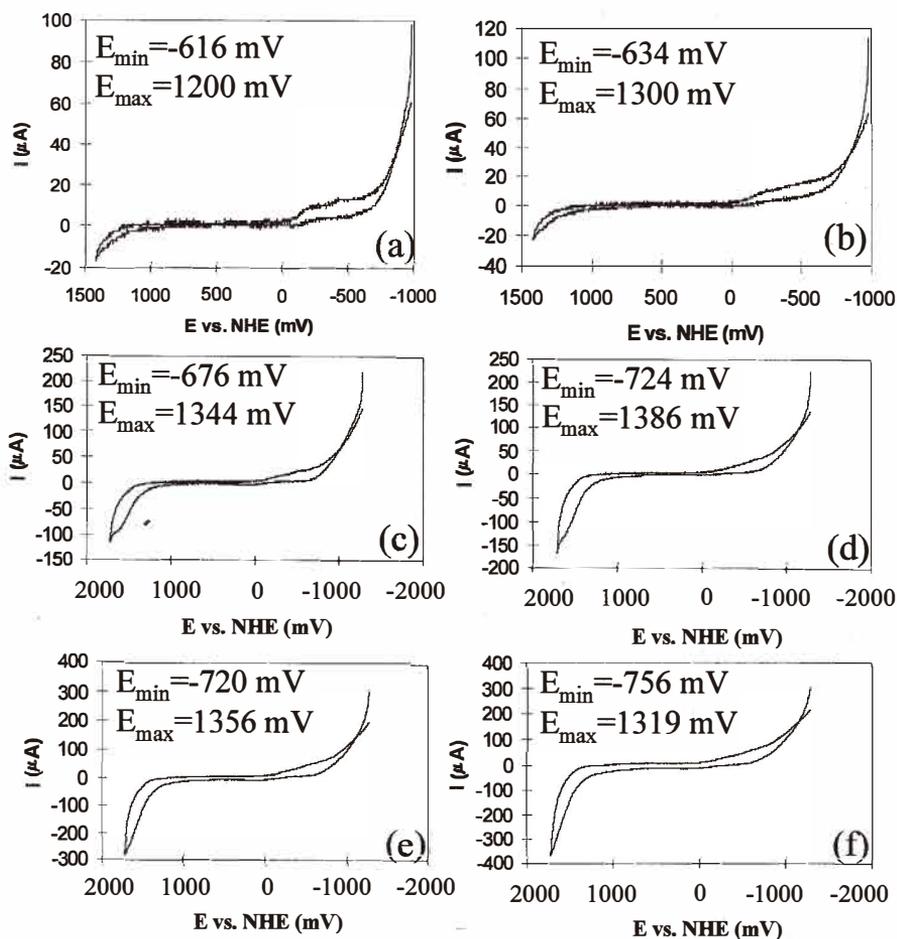


Fig. 2. Background cyclic voltammetric behavior of highly conducting boron-doped diamond in a supporting electrolyte of 0.5 M NaCl. Scan rate: (a) 10, (b) 25, (c) 50, (d) 100, (e) 500 and (f) 1000 mV/s. These data are corrected for uncompensated IR. The apparent area of the electrode is 0.71 cm² (effective area: ~0.82 cm²). Reference electrode: Ag/AgCl (0.5 M NaCl). X-axis shows potential vs normal hydrogen electrode (E vs NHE).

background current will be on the order of picoamperes if the electrode size is reduced by 10⁶ times. In such a case, the electrode size will be on the order of 8.4 × 8.4 μm². This indicates that the microdiamond electrode can be used to detect dopamine neurotransmitters at picomolar levels.

Figure 3 shows the cyclic voltammograms for different concentrations of dopamine (0.01, 0.1, 1 and 5 mM) at various scan rates ranging from 10 to 1000 mV/s. The data

shown in Fig. 3 are corrected for uncompensated IR, and its respective background current, as shown in Fig. 2, has been subtracted. The a_1 and a_2 peaks correspond to the oxidation process of dopamine to dopamine o-quinone and indole to aminochrome, respectively. The c_1 and c_2 peaks correspond to the reduction of dopamine o-quinone to dopamine and aminochrome to indole, respectively. Table 1 shows the data on peak separation (ΔE_p) and peak currents (i_{pa} and i_{pc}), extracted from the experimental data shown in Figs. 3 (a)–(f). An increase in ΔE_p with increasing scan rate is characteristic of an irreversible process. The current corresponding to the dopamine o-quinone to aminochrome redox reaction strongly depends on the dopamine concentration. The current corresponding to the dopamine/dopamine o-quinone redox couple dominates over those of other couples such as dopamine o-quinone and aminochrome at higher concentrations of dopamine (for example, 1 mM and 5 mM). We do not have a suitable explanation to support this observation at this time. The number of electrons transferred in the reaction shown in Fig. 1 for the first reversible couple is 2 and is the same for the second reversible couple.⁽²⁾ This was determined from the separation of the peak potentials in the cyclic voltammogram. The ΔE_p (Tables 1a and 1b) values in Fig. 3 are significantly higher than the predicted values, such as ~ 29.5 mV, for a reversible two-electron transfer reaction. This indicates the occurrence of irreversible electron transfer kinetics at the diamond electrode surface. The ratio of the peak currents deviates from unity, which indicates the irreversibility of the electrode process. The current response increased with an increase in the concentration of redox species in the solution and also with the scan rate at a constant concentration. This is due to an increase in the concentration of reactive species at the electrode/solution interface, which can undergo the electron-transfer reaction. Table 1 (a and b) also exhibits the heterogeneous electron transfer rate constants that were determined using experimental data such as peak-potential separation for each redox couple [1 and 2] and respective parameters such as peak currents and concentration, which were extracted from Fig. 3.^(26,27) The heterogeneous electron transfer rate constant has been determined using the experimental data and COOL algorithm. The rate constant k^0 for redox couples 1 and 2 was found to be in the range of 10^{-8} – 10^{-11} cm/s. Therefore, this reaction may be considered to be an irreversible process at the diamond electrode-solution interface.

The concentrations of dopamine in the brain, kidneys and other parts of the human body will be in the picomolar range. We employed an electrode of 0.71 cm² area and were able to detect 0.01 mM (10 μ M) in this preliminary experiment by voltammetry. We assume that we could reduce the electrode size by 10^6 times by patterning of the diamond; therefore, the background current will be reduced by 10^6 times. Figure 4 shows a scanning electron micrograph of a selectively deposited polycrystalline diamond thin film square (~ 300 μ m²) on a silicon substrate.⁽²⁸⁾ There exists an insignificant background current for the diamond electrode, as evidenced in Fig. 2. It may be possible to detect picomolar concentrations for longer periods of time using robust doped diamond electrodes that are highly stable, if they significantly retain electrochemical activity. This study clearly showed that two electrochemical charge transfer reactions that are occurring at the diamond electrode during the electrochemical oxidation of dopamine can be detected. The voltammetric features in our study corresponding to dopamine to dopamine o-quinone and dopamine o-quinone to aminochrome reactions are highly reproducible, although the peak

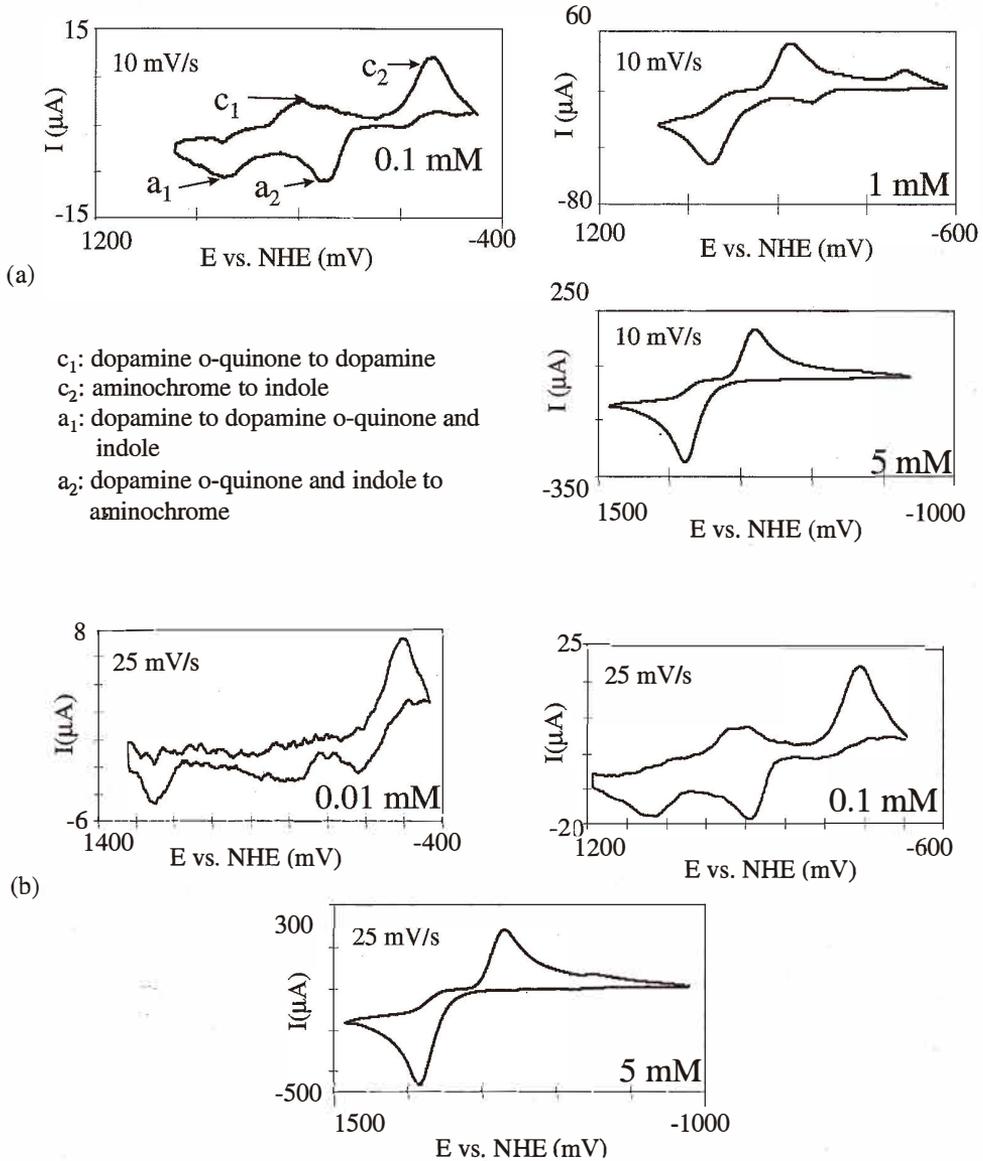


Fig. 3. Cyclic voltammetric behavior of highly conducting boron-doped diamond in 0.5 M NaCl supporting electrolyte containing various concentrations (0.01 to 5 mM) of dopamine, at various scan rates ranging from 10 to 1000 mV/s. The apparent area of the electrode is 0.71 cm² (effective area: ~0.82 cm²). Reference electrode: Ag/AgCl (0.5 M NaCl).

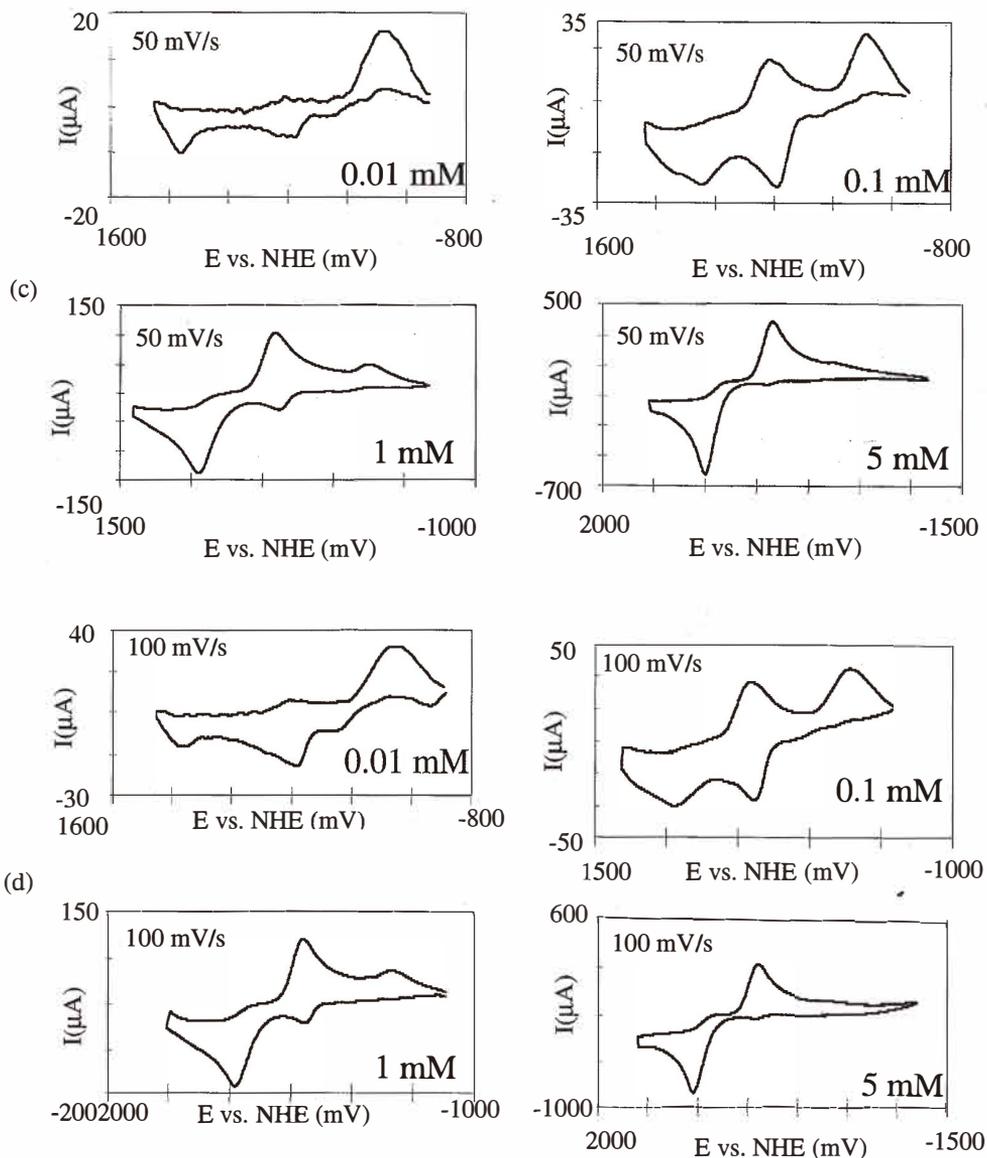


Fig. 3. (continued) Cyclic voltammetric behavior of highly conducting boron-doped diamond in 0.5 M NaCl supporting electrolyte containing various concentrations (0.01 to 5 mM) of dopamine, at various scan rates ranging from 10 to 1000 mV/s. The apparent area of the electrode is 0.71 cm^2 (effective area: $\sim 0.82 \text{ cm}^2$). Reference electrode: Ag/AgCl (0.5 M NaCl).

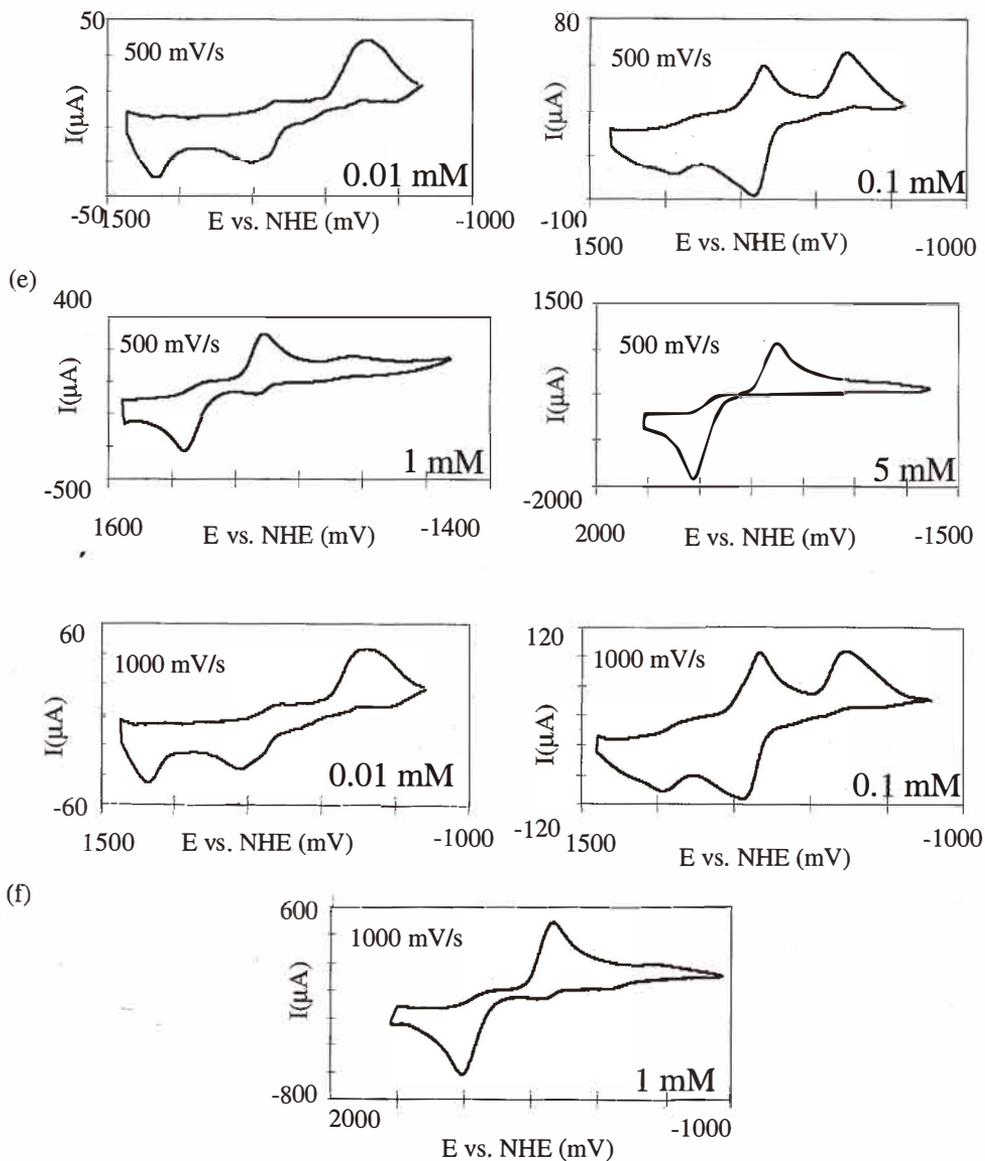


Fig. 3. (continued) Cyclic voltammetric behavior of highly conducting boron-doped diamond in 0.5 M NaCl supporting electrolyte containing various concentrations (0.01 to 5 mM) of dopamine, at various scan rates ranging from 10 to 1000 mV/s. The apparent area of the electrode is 0.71 cm^2 (effective area: $\sim 0.82 \text{ cm}^2$). Reference electrode: Ag/AgCl (0.5 M NaCl).

Table 1a

Cyclic voltammetric studies of highly conducting boron-doped diamond in 0.5 M NaCl supporting electrolyte containing dopamine ranging from 0.01 mM to 5 mM at scan rates ranging from 10 mV/s to 1000 mV/s, for the first redox couple (dopamine to dopamine o-quinone and indole). ΔE_p = peak separation; I_p = peak current; k^0 = heterogeneous reaction rate constant; $E^{0'}$ = $[E_p(c) + E_p(a)]/2$.

Scan rate (mV/s)	Dopamine concentration (mM)	$E_p(c_1)$ (mV)	$E_p(a_1)$ (mV)	ΔE_p (mV)	$E^{0'}$ (mV)	$I_p(c_1)$ (μA)	$I_p(a_1)$ (μA)	k^0 (cm/s)	$\frac{I_p(a_1)}{I_p(c_1)}$
1000	1	344	1014	670	679	481	-625	3.4×10^{-8}	1.3
	0.1	336	982	646	659	84	-102	9.3×10^{-8}	1.2
	0.01	312	1184	872	748	6	-45	8.2×10^{-10}	7.5
500	5	260	1066	806	663	1129	-1851	1.1×10^{-9}	1.6
	1	384	1012	628	698	295	-430	4.3×10^{-8}	1.5
	0.1	346	948	602	647	50	-71	1.3×10^{-7}	1.4
	0.01	342	1170	828	756	5	-40	1.6×10^{-9}	8.0
100	5	400	1046	646	723	519	-847	1.2×10^{-8}	1.6
	1	408	956	548	682	138	-185	1.0×10^{-7}	1.3
	0.1	416	948	532	682	36	-40	3.7×10^{-7}	1.1
	0.01	412	1158	746	785	5	-16	7.9×10^{-9}	3.2
50	5	356	1002	646	679	384	-622	8.5×10^{-9}	1.6
	1	410	946	536	678	103	-139	9.7×10^{-8}	1.3
	0.1	426	898	472	662	21	-28	6.9×10^{-7}	1.3
	0.01	424	1142	718	783	2	-10	5.5×10^{-9}	5.0
25	5	352	924	572	638	280	-466	2.6×10^{-8}	1.7
	0.1	442	864	422	653	7	-18	6.1×10^{-7}	2.6
	0.01	-	1088	-	-	-	-	-	-
10	5	400	886	486	643	183	-300	9.2×10^{-8}	1.6
	1	430	874	444	652	40	-65	2.3×10^{-7}	1.6
	0.1	478	874	396	676	5	-11	7.2×10^{-7}	2.2

separations were large compared to the expected thermodynamic values of close to 29.5 mV. This also indicates that the kinetics of electron transfer reactions of dopamine/aminochrome at the diamond electrode solution interface is slow.

Table 1b

Cyclic voltammetric studies of highly conducting boron-doped diamond in 0.5 M NaCl supporting electrolyte containing dopamine ranging from 0.01 mM to 5 mM, at scan rates ranging from 10 mV/s to 1000 mV/s, for the second redox couple (dopamine o-quinone and indole to aminochrome). ΔE_p = peak separation; I_p = peak current; k^0 = heterogeneous reaction rate constant; $E^{0'}$ = $[E_p(c) + E_p(a)]/2$.

Scan rate (mV/s)	Dopamine concentration (mM)	$E_p(c_2)$ (mV)	$E_p(a_2)$ (mV)	ΔE_p (mV)	$E^{0'}$ (mV)	$I_p(c_2)$ (μ A)	$I_p(a_2)$ (μ A)	k^0 (cm/s)	$\frac{I_p(a_2)}{I_p(c_2)}$
1000	5	-512	436	948	-38	199	-62	6.2×10^{-11}	0.31
	0.1	-248	442	690	97	87	-112	4.1×10^{-8}	1.29
	0.01	-340	550	890	105	43	-36	4.1×10^{-9}	0.84
500	5	-	-	-	-	-	-	-	-
	1	-312	438	750	63	157	-79	2.3×10^{-9}	0.50
	0.1	-216	408	624	96	64	-96	1.1×10^{-7}	1.50
	0.01	-374	494	868	60	38	-31	5.6×10^{-9}	0.82
100	5	-220	426	646	103	169	-44	3.8×10^{-9}	0.26
	1	-330	378	708	24	71	-42	2.4×10^{-9}	0.59
	0.1	-308	382	690	37	45	-36	2.1×10^{-8}	0.80
	0.01	-348	368	716	10	32	-25	9.1×10^{-8}	0.78
50	5	-256	398	654	71	123	-27	2.3×10^{-9}	0.22
	1	-260	380	640	60	50	-29	6.3×10^{-9}	0.58
	0.1	-244	376	620	66	30	-28	5.5×10^{-8}	0.93
	0.01	-324	372	696	24	16	-7	6.7×10^{-8}	0.44
25	5	-242	-	-	-	85	-	-	-
	0.1	-182	380	562	99	24	-19	1.4×10^{-7}	0.79
	0.01	-190	328	518	69	7	-3	9.4×10^{-7}	0.43
10	5	-	-	-	-	-	-	-	-
	1	-216	308	524	46	18	-10	2.2×10^{-8}	0.56
	0.1	-174	370	544	98	14	-12	1.1×10^{-7}	0.86

4. Conclusions

We have reported the growth of boron-doped diamond over the molybdenum substrate by a microwave plasma CVD process using hydrogen along with methane as a carbon source. Cyclic voltammograms showed that the diamond electrode material is stable over a wide potential range in aqueous solutions of supporting electrolytes such as 0.5 M NaCl. It may be qualitatively concluded that, based on the stability characteristics observed in cyclic voltammetry studies, diamond electrodes may be useful in bioelectroanalytical chemistry. We investigated the redox kinetics of dopamine in a supporting electrolyte of 0.5 M NaCl solution. The nature of the redox kinetics over the diamond electrode is electrochemically irreversible. The observed peak separation was found to be significantly greater than the characteristic peak separation (29.5 mV) corresponding to two electron-transfer reaction kinetics of (redox couple 1) dopamine/dopamine o-quinone and (redox couple 2) dopamine o-quinone and indole/aminochrome redox couples. Redox kinetics of dopamine/aminochrome at the boron-doped diamond electrode has clearly shown two voltammetric features for each redox couple in our cyclic voltammetric data. We assume that this is possible to observe only when the working electrode has a high electrical conductivity and wide usable potential range with an insignificant background current, as evidenced in our studies. We were able to detect a 0.01 mM level of dopamine at the diamond electrode. We anticipate that it will be possible to detect very low concentrations of dopamine (picomolar) using microdiamond electrodes, as shown in Fig. 4. This would

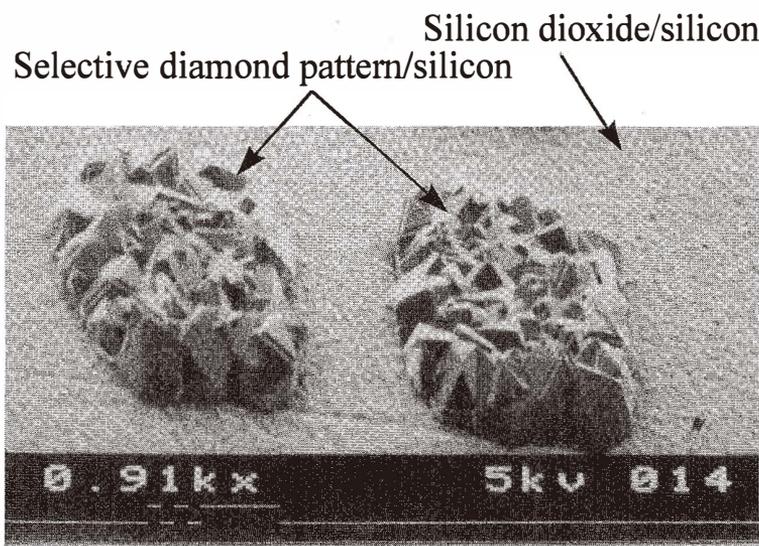


Fig. 4. Scanning electron micrograph of a selectively deposited polycrystalline diamond thin film square ($\sim 300 \mu\text{m}^2$) on a silicon substrate.

pave the way to *in vivo* detection of very low concentrations of dopamine using robust microdiamond electrodes which may eventually be used as an electrode material for bioelectrochemical detection.

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References

- 1 J. E. Field: The Properties of Diamond (Academic Press, London, 1979).
- 2 Voltammetry in the Neurosciences, Principles, Methods and Applications, ed. J. B. Justice, Jr. (Humana Press, New Jersey, USA, 1987) p. 34.
- 3 H. E. Zittel and F. J. Miller: Anal. Chem. **37** (1965) 200.
- 4 D. T. Fagan, I. F. Hu and T. Kuwana: Anal. Chem. **57** (1985) 2759.
- 5 R. L. McCreery and K. K. Cline: Carbon Electrodes in Laboratory Techniques in Electroanalytical Chemistry, ed. P. T. Kissinger and W. R. Heineman, 2nd edition (Marcel Dekker, Inc., New York, 1996) p. 293.
- 6 M. Poon and R. L. McCreery: Anal. Chem. **58** (1986) 2745.
- 7 A. G. Ewing and R. M. Wightman: J. Neurochem. **43** (1984) 570.
- 8 A. G. Ewing, J. C. Bigelow and R. M. Wightman: Science **221** (1983) 169.
- 9 W. G. Kuhr, A. G. Ewing, W. L. Caudill and R. M. Wightman: J. Neurochem. **43** (1984) 560.
- 10 A. W. Sternson, R. McCreery, B. Feinberg and R. N. Adams: Electroanal. Chem. and Interfacial Electrochem. **46** (1973) 313.
- 11 M. D. Hawley, S. V. Tatawawadi, S. Piekarski and R. N. Adams: J. Amer. Chem. Soc. **89** (1967) 447.
- 12 D. C. S. Tse, R. L. McCreery and R. N. Adams: J. Medicinal Chem. **19** (1976) 37.
- 13 R. N. Adams: Anal. Chem. **48** (1976) 1128.
- 14 J. L. Ponchon, R. Cesuglio, F. Gonon, M. Jouvet and J. F. Pujol: Anal. Chem. **51** (1979) 1483.
- 15 M. E. Rice and C. Nicholson: Anal. Chem. **61** (1989) 1805.
- 16 R. Ramesham, R. F. Askew, M. F. Rose and B. H. Loo: J. Electrochem. Soc. **140** (1993) 3018.
- 17 S. Alehashem, F. Chambers, J. Strojek, G. M. Swain and R. Ramesham: Anal. Chem. **67** (1995) 2812.
- 18 J. W. Strojek, M. C. Granger, G. M. Swain, T. Dalla and M. W. Holtz: Anal. Chem. **68** (1996) 2031.
- 19 R. Ramesham and M. F. Rose: Thin Solid Films **300** (1997) 144.
- 20 R. Ramesham and M. F. Rose: "Electrochemical Impedance Spectroscopy, DC Polarization and Cyclic Voltammetric Behavior of Microwave Plasma and Hot Filament CVD Diamond Coated Mo, Mo, and Pt Substrate Materials" Fall (1996) MRS Symposium Proceedings, Symposium P (1997) p. 561.

- 21 R. Ramesham and M. F. Rose: *Diamond and Related Materials* **6** (1997) 17.
- 22 R. Ramesham, T. Roppel, C. Ellis, D. A. Jaworske and W. Baugh: *J. Mater. Res.* **6** (1991) 1278.
- 23 R. Ramesham, T. Roppel, C. Ellis and B. H. Loo: *J. Electrochem. Soc.* **138** (1991) 2981.
- 24 R. Ramesham: *Thin Solid Films* **229** (1993) 44.
- 25 H. B. Martin, A. Argoitia, U. Landau, A. B. Anderson and J. C. Angus: *J. Electrochem. Soc.* **143** (1996) L133.
- 26 A. J. Bard and L. R. Faulkner: *Electrochemical Methods: Fundamentals and Applications* (John Wiley & Sons, New York, 1980) 6th Chapter.
- 27 R. S. Nicholson and I. Shain: *Anal. Chem.* **36** (1964) 706.
- 28 R. Ramesham, T. Roppel, C. Ellis and D. A. Jaworske: *J. Mater. Res.* **6** (1991) 1278.