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Preliminary Study of Ferri-Ferrocyanide Redox Kinetics at the Submillimeter Boron-Doped CVD Diamond Electrode

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Boron-doped CVD diamond was grown on mechanically damaged and cleaned molybdenum substrate using the microwave plasma chemical vapor deposition (CVD) process. The gases used to grow the CVD diamond were methane and hydrogen. Boron doping of the diamond was achieved *in situ* using a solid disk source of B_2O_3. The submillimeter boron-doped CVD diamond electrode was evaluated for background current response in 0.5 M NaCl by cyclic voltammetry. Photolithography was used to pattern the CVD diamond in order to fabricate a submillimeter electrode for cyclic voltammetry studies. Preliminary results on the voltammetric response of the fabricated (0.003 cm^2) CVD diamond electrode are reported. We have observed negligible background current for submillimeter boron-doped CVD diamond electrode over a wide potential range. Decomposition of water occurs electrochemically, evolving O_2 during positive (anodic) polarization and H_2 during negative (cathodic) polarization. Scanning electron microscopy has been used to study the morphology of the diamond electrode before and after electrochemical characterization; we conclude qualitatively that the morphology was unchanged. We have investigated the redox kinetics of ferri-ferrocyanide ($Fe(CN)_6^{3-} + e^- \Leftrightarrow Fe(CN)_6^{4-}$) in 0.5 M NaCl solution at various scan rates (1 mV/s to 20,000 mV/s). The reaction is reversible at the diamond electrode, but the redox kinetics are slow. The results of cyclic voltammetry using submillimeter boron-doped CVD diamond electrode reveal a change in shape of the voltammetric response curve from sigmoidal to peak-shaped as a function of scan rate, reflecting the change in the diffusion layer thickness.

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1. Introduction

Diamond is a unique material with innumerable applications due to its unusual combination of physical and chemical properties.[1] Several potential applications are anticipated for diamond in electronics, optics, corrosion-resistant coatings, electrochemical sensors and electroanalytical chemistry.

Glassy carbon, highly oriented pyrolytic graphite (HOPG), platinum, dropping mercury electrodes (DME), carbon paste, carbon nanotube, graphite, silver and gold are the materials of general interest for electroanalytical use, since they have a wide potential range for electroanalytical use in acidic solutions. The limitations of DME are its toxicity and mechanical instability. The main advantages of solid-state electrodes are a wide-potential range, mechanical stability, electrocatalytic activity, adsorptivity, reproducibility and ease of use. This makes them more useful than DME. The slow oxidation kinetics of diamond lead to a wide and useful working potential range over other conventional materials with a markedly low background current. A submicron solid-state electrode that requires no chemical and mechanical pretreatments to regenerate the clean surface is necessary for reliable and reproducible electrochemical and bioelectrochemical sensor applications. Microelectrodes are a prerequisite for the advancement of electrochemistry in microenvironmental studies of localized corrosion (pitting corrosion, crevice corrosion, etc.), toxic metal ion detection in small volumes, membrane pores and single biological cells. Common microelectrode materials found in the literature are Pt, Au, Ag, Hg, carbon fiber, glassy carbon and graphite.[2-4]

The main advantages of microelectrodes are the large ratio of faradaic current to nonfaradaic current and low resistance-to-area ratio. Nonfaradaic currents at the microelectrodes are proportional to electrode area; therefore, the faradaic/nonfaradaic current ratio can be increased by making the electrode dimensions (0.003 cm^2) small. This is the most important advantage of microelectrodes in analytical applications. The disadvantages of microelectrodes are unpredictability of surface effects, irreproducibility of geometry, detection of very low level background currents, and low faradaic efficiencies. Microelectrodes have several uses in biomedical, analytical, kinetic and electrolytic applications. The small magnitude of uncompensated IR effect in solutions with microelectrodes permits studies using lower conductivity media. Microelectrodes may be employed in experiments that use a high-resistivity solution in which there is little or no supporting electrolyte. The absence of supporting electrolyte can prevent problems caused by impurities introduced with the electrolyte. The absence of supporting electrolyte will also significantly extend the range of potential useful for electrochemical measurements. Microelectrodes may have use in low-dielectric media as sensors for analyzing trace electroactive components which may be present as a result of wear products and container materials for fuels and lubricants. Microelectrodes also enable electrochemical studies in nonpolar solvents. Microelectrodes exhibit a fast response time and attain steady-state polarization in a very short time. Ultrafast cyclic voltammetry (sweep rate: kV/s) plays a very important role in measurements with microelectrodes by offering very low detection limits with an extremely short time required for a single scan.

Cyclic voltammetry is the most useful electroanalytical technique for the study of

electroactive species. The working electrode plays a critical role in the electrochemical experiments. Reactions of interest take place at the working electrode which is usually constructed of chemically inert and possibly catalytic material.

There have been some reports on the characterization of diamond films by electrochemical techniques. Ramesham *et al.*[5] have demonstrated the growth of polycrystalline diamond on glassy carbon and graphite electrode materials for use in applied electrochemistry and electroanalytical chemistry. Swain and Ramesham,[6] Swain,[7] Alehashem *et al.*[8] and Zhu *et al.*[9] have reported the cyclic voltammetric behavior of ferri-ferrocyanide using boron-doped diamond films. Ramesham and Rose[10] have recently shown that the diamond electrode is stable over a wide potential range, allowing the decomposition of H_2O to occur and the evolution of hydrogen and oxygen during cathodic and anodic polarizations, respectively in various electrolytes. Miller *et al.*[11] have reported the cyclic voltammetric behavior of ferri-ferrocyanide using cobalt-ion-implanted diamond electrode. Ramesham and Rose[12,13] have reported the electrochemical behavior of doped-polycrystalline diamond in 0.5 M NaCl solution using electrochemical AC impedance spectroscopy and DC polarization techniques. Voltammetric features of Ce^{3+}/Ce^{4+} were observed using the diamond electrode, and the redox process was found to be completely irreversible.[14]

Good-quality polycrystalline diamond films have been grown using less than 1% methane in hydrogen at a pressure of 30 – 40 Torr.[15] Boron-doped diamond film is electrically conducting[16,17] and a submillimeter diamond electrode was fabricated to investigate the electrode characteristics using slow to fast scan cyclic voltammetry. Voltammetry using the submillimeter boron-doped diamond electrode may have significant practical use in the field of electroanalytical chemistry. We refer to submillimeter boron-doped diamond electrode as diamond electrode in the remaining text for the sake of simplicity. In this study, we will demonstrate the fabrication of a small conducting diamond electrode and characterize the background current response in 0.5 M NaCl solution at various scan rates. We will also report the redox kinetic behavior of ferri-ferrocyanide at the diamond electrode in 0.5 M NaCl as a supporting electrolyte. To our knowledge, this is the first report on the electrochemical voltammetric response for a diamond electrode using slow to fast scan cyclic voltammetry.

2. Experimental Details

Surface damaging was a necessary to nucleate CVD diamond on non-diamond substrates. Molybdenum substrates were mechanically pretreated with 0.25 – 60 μm diamond paste and washed with tap water, acetone, methanol and deionized water.[15–17]

A microwave plasma (2.45 GHz) assisted CVD system (ASTeX) was used to grow the diamond films. A schematic diagram of the diamond deposition system has been described earlier.[15] The substrate was placed at the center of a stage which was then loaded into a quartz bell jar reactor. The reactor 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, and microwave power, and by waveguide tuning. The substrate was heated *in situ* by the

microwave plasma to attain the desired substrate temperature before initiating the growth of diamond. Ultrahigh-purity grade hydrogen and research-grade methane were used in our experiments. The temperature was monitored remotely by an optical pyrometer. Diamond deposition was started by injecting methane into the system when the substrate reached the desired temperature. The deposition rate under the conditions listed in Table 1 was 1–0.5 μm/h. A continuous film of diamond was obtained after 10 to 20 h of growth.

Boron doping of diamond film was achieved by using a solid disk source consisting of B_2O_3 and other oxides. The solid boron disk source was used as a base to the substrate during growth of *in situ* doped diamond at substrate temperatures ranging from 945 to 982°C. The size (30 mm × 30 mm) of the boron disk source was greater than that of the substrate (21 mm × 21 mm), such that the doping disk source could be exposed to hydrogen and methane microwave plasma, subsequently raising the temperature and creating sufficient vapor pressure of atomic boron around the disk to enable *in situ* doping of diamond. We have measured the electrical resistivity of boron-doped diamond samples 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 in the order of 1,000 ppm. Deposition conditions are given in Table 1.[17]

Initially, polycrystalline diamond was grown over the molybdenum substrate for 17.25 h and photolithography was used to fabricate the diamond electrode. Figure 1 shows the schematic cross-sectional diagram of the fabricated diamond electrode for voltammetric characterization.

All solutions were prepared using reagent-grade chemicals and deionized water. Cyclic voltammograms were obtained at various scan rates of 1 mV/s to 20,000 mV/s. The exposed apparent area of the diamond electrode was 0.003 cm^2 for the polycrystalline diamond. The true area of the electrode as corrected for surface roughness, was 0.00345 cm^2.[18] The reference electrode used in this study was Ag | AgCl | 0.5 M NaCl. The potential of the reference electrode for 0.5 M NaCl with respect to the standard hydrogen electrode (SHE) was ~0.240 V vs SHE. A platinum foil counter electrode was used during

Table 1
Experimental parameters for the deposition of very low-resistivity boron-doped CVD diamond by microwave plasma on molybdenum substrate.

Pressure, Torr	33.2 (or 4.415 kPascals)
H_2 flow, sccm	500
CH_4 flow rate, sccm	3.6
% CH_4 in $CH_4 + H_2$	0.71
Substrate temperature, °C	945 – 982
Substrate area, cm^2	4.4
Growth time, h	17.25
Growth rate (μm/h)	0.5 – 1
Forward power, W	750
Reflected power, W	< 2
Substrate base (area)	B_2O_3 disk (~9 cm^2)

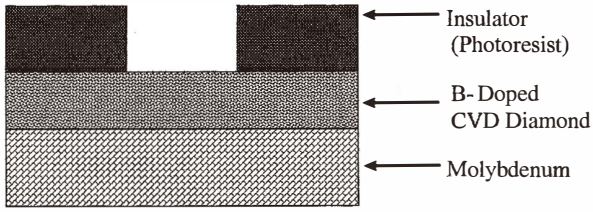

Fig. 1. Schematic diagram of the diamond electrode prepared for background characterization and redox kinetics of ferro-ferricyanide by cyclic voltammetry.

the electrochemical measurements. All electrochemical experiments were conducted at room temperature. The solution was exposed to air during electrochemical measurements. A simple three-electrode (test electrode, counter electrode, reference electrode), single-compartment electrochemical cell was used in this study. A potentiostat (EG & G Model 273) was used to perform cyclic voltammetry experiments. The experimental data were not corrected for IR compensation. The solution was not stirred during the voltammetry experiments.

3. Results and Discussion

Figure 2(a) shows the well-faceted morphology of the diamond film after electrochemical testing. The morphology of the diamond was not changed after several electrochemical experiments. This is a significant observation although it was expected for the diamond. The films grown by microwave plasma CVD process under similar experimental conditions have been analyzed earlier by Raman spectroscopy.[5,15–17] Profilometric measurements reveal that the roughness factor of the diamond electrode varies from 0.1 to 1 μm.[15] A 15% area correction was made for surface roughness based on the diamond crystallite dimension of 0.1 μm.[18] The apparent area of the electrode was 0.003 cm^2. The area of the electrode was constant in all the experiments reported in this paper. Photolithography was used to fabricate the submillimeter diamond electrode using thick photoresist as shown in Fig. 2(b) by scanning electron microscopy. Figure 2(c) shows the micrograph of the reduced electrode size performed manually using photoresist. Thick photoresist was used as an insulator during electrochemical measurements.

Figures 3(a) – 3(h) show the cyclic voltammetric behavior of the submillimeter diamond electrode in 0.5 M NaCl at various scan rates ranging from slow (25 mV/s) to fast (10,000 mV/s). The data shown in Fig. 3 are not corrected for uncompensated IR drop. The diamond electrode potential was measured with reference to a reference electrode (RE), and was plotted in Fig. 3 as the x-axis. The observed current during the polarization was plotted as the y-axis in Fig. 3. The diamond electrode was electrochemically stable over a potential range of +1.2 to –1.7 V vs R.E. (R.E. potential: 0.24 V vs NHE). No significant decomposition of water occurred over a wide potential range. The observed

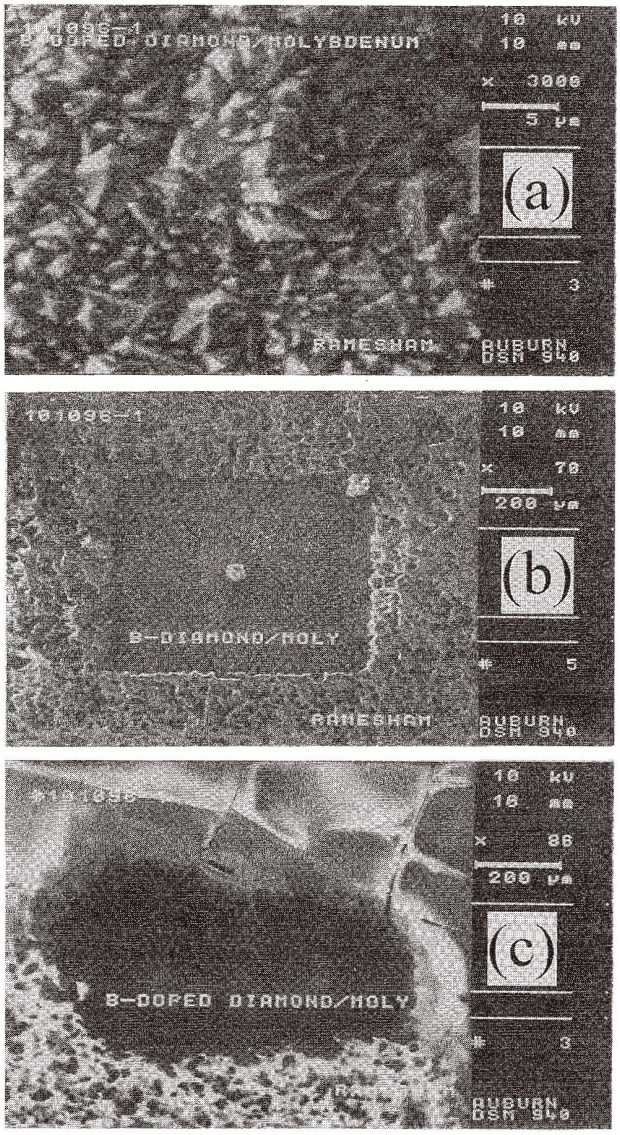

Fig. 2. Scanning electron micrographs of (a) electrochemically tested diamond electrode in 0.5 M NaCl as supporting electrolyte, (b) fabricated diamond electrode by photolithography and (c) diamond electrode shown in "b" whose size was manually further reduced. Photoresist was used as an insulator.

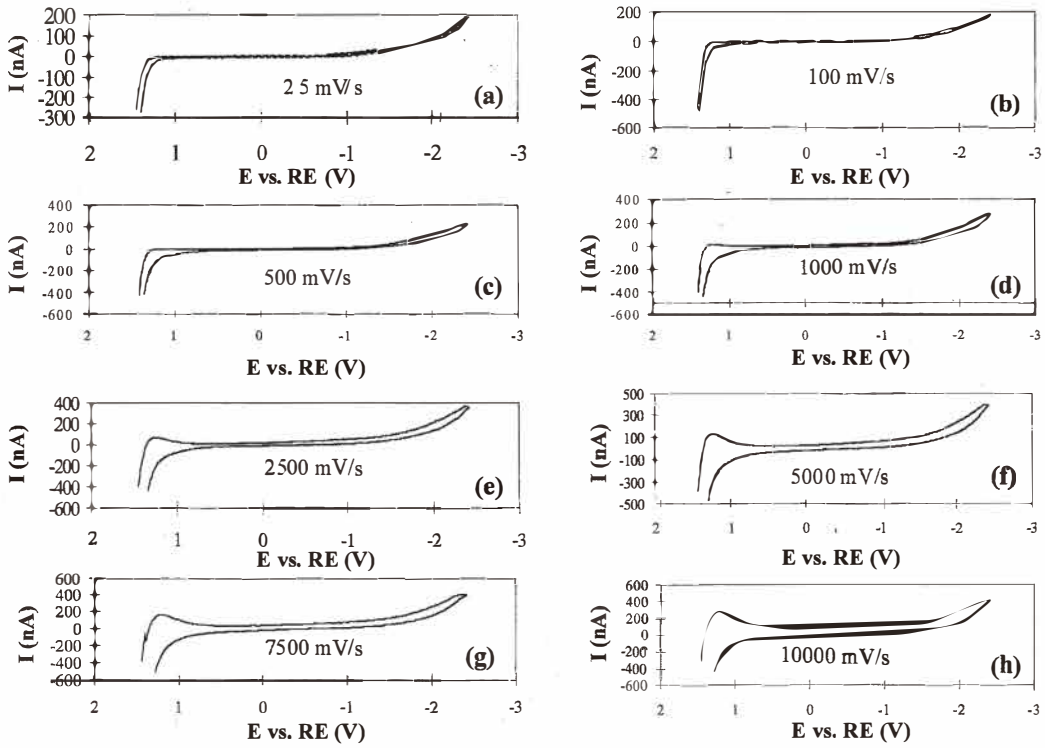

Fig. 3 Background cyclic voltammetric behavior of diamond electrode in 0.5 M NaCl as the supporting electrolyte without IR compensation at various scan rates. (a) 25 mV/s, (b) 100 mV/s, (c) 500 mV/s, (d) 1,000 mV/s, (e) 2,500 mV/s, (f) 5,000 mV/s, (g) 7,500 mV/s and (h) 10,000 mV/s. Apparent area of the electrode was 0.003 cm^2 (area of the electrode after surface roughness correction: 0.00345 cm^2). Reference electrode: Ag|AgCl|0.5 M NaCl.

background current was in the range of 5 – 6 nA and was lower than that of conventional materials such as platinum and glassy carbon, even during fast scan voltammetry. Taking into consideration the inherent advantages of microelectrodes, this feature will certainly aid in the use of the diamond electrodes for fast scan voltammetry. This feature will also be advantageous in investigations of redox kinetics in electroanalytical chemistry. To our knowledge, this is the first report of the voltammetric response at the submillimeter diamond electrode/solution interface. The potential ranges provided in this paper are values within ±50 mV. We did not measure the pH of the solution.

Figure 4 shows the cyclic voltammetric behavior of conducting diamond electrode at various scan rates in 0.5 M NaCl solution containing 4 mM $K_3Fe(CN)_6$. ΔE_p is defined as separation of anodic and cathodic peaks in a cyclic voltammogram. The ΔE_p decreased as the scan rate decreased, although this value was higher than expected. This could be due to

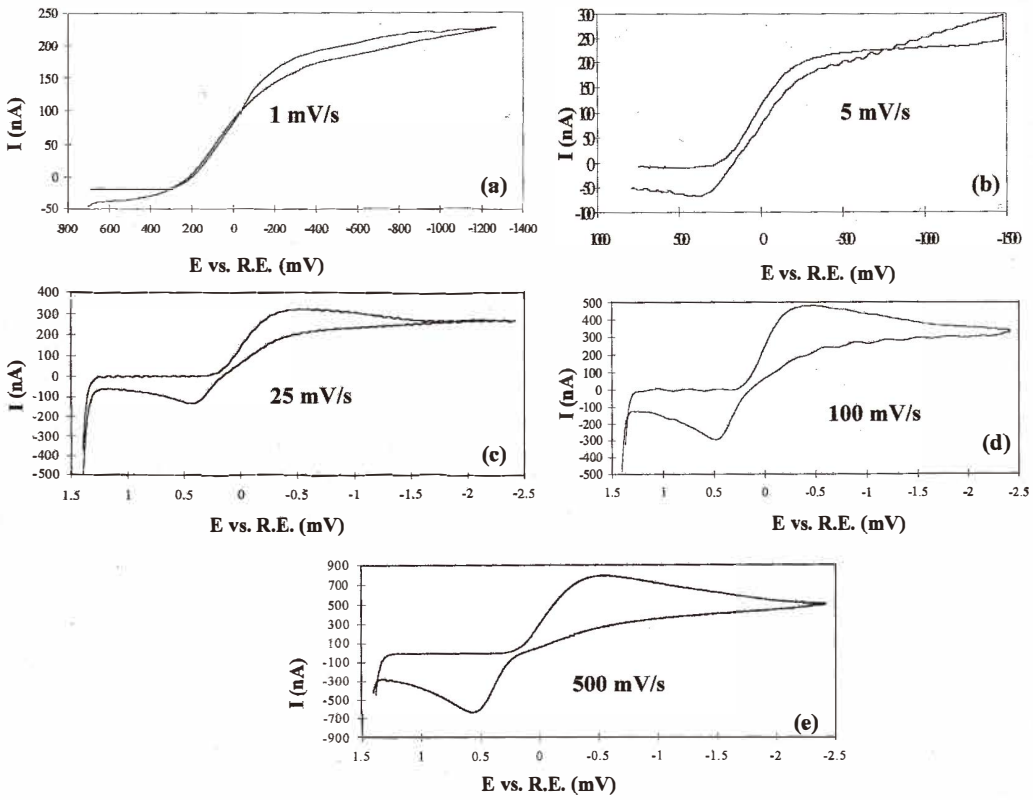

Fig. 4(a)–(e). Cyclic voltammetric behavior of diamond electrode in 0.5 M NaCl solution containing 4 mM $K_3Fe(CN)_6$ at scan rates of (a) 1 mV/s, (b) 5 mV/s, (c) 25 mV/s, (d) 100 mV/s and (e) 500 mV/s. The data in (a) and (b) were not corrected for background current response. The data in (c) to (e) were corrected for the background current response shown in Figs. 3(a) to 3(c). Apparent area of the electrode was 0.003 cm^2 (area of the electrode after surface roughness correction: 0.00345 cm^2). Reference electrode: Ag | AgCl | 0.5 M NaCl.

the slow electron transfer reaction kinetics at the diamond electrode or high electrical resistivity of diamond. The data shown in Fig. 4 were corrected for background current response shown in Fig. 3. We did not record any background current response for 1 mV/s, 5 mV/s and 20,000 mV/s. Therefore, the data shown in Figs. 4(a), 4(b) and 4(k) were not corrected for background current response. Figures 4(a) and 4(b) show a sigmoidal shape of the cyclic voltammogram for the ferri-ferrocyanide redox couple. The extent by which the planar or radial component dominates depends on the relative dimensions of the electrode and diffusion layer thickness, as expressed by the dimensionless parameter $(Dt)^{1/2}/r^2$, where t is the electrolysis time and r is the smallest dimension of the electrode. If the

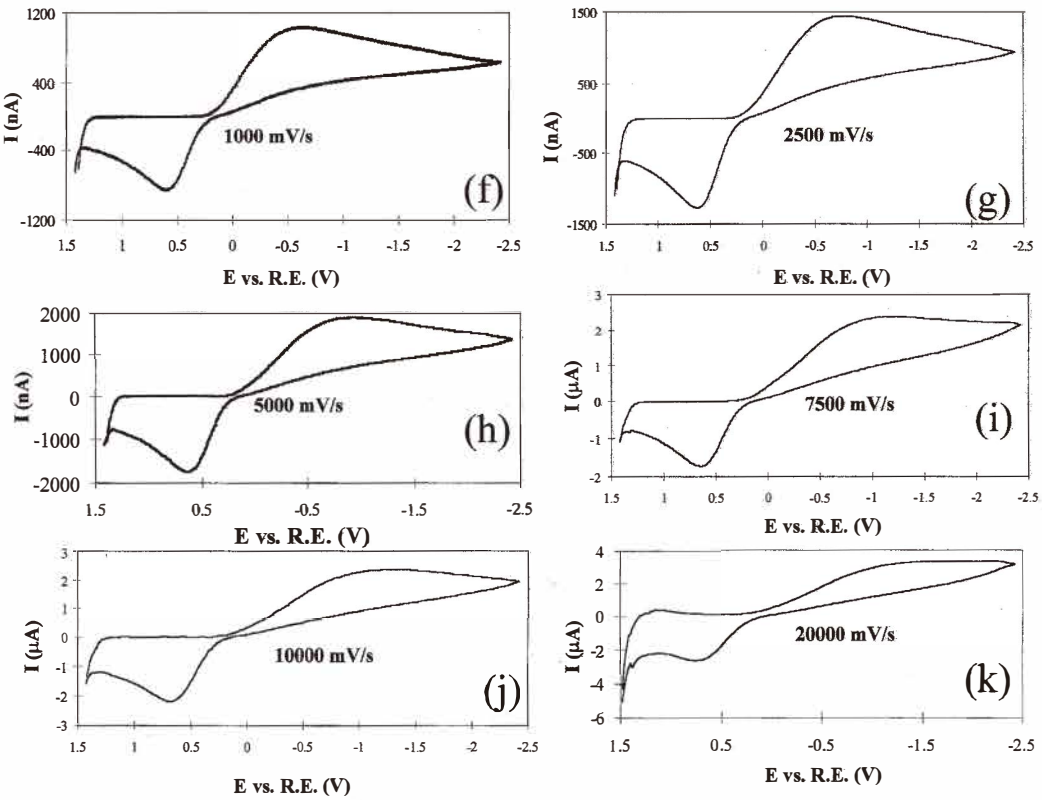

Fig. 4(f)–(k). Cyclic voltammetric behavior of diamond electrode in 0.5 M NaCl solution containing 4 mM $K_3Fe(CN)_6$ at scan rates of (f) 1,000 mV/s, (g) 2,500 mV/s, (h) 5,000 mV/s, (i) 7,500 mV/s, (j) 10,000 mV/s and (k) 20,000 mV/s. The data in (k) was not corrected for background current response. The data in (f) to (j) were corrected for the background current response shown in Fig. 3 (d) to 3(h). Apparent area of the electrode was 0.003 cm^2 (area of the electrode after surface roughness correction: 0.00345 cm^2). Reference electrode: Ag | AgCl | 0.5 M NaCl.

value of $(Dt)^{1/2}/r^2$ is greater than 1, where the diffusion layer thickness exceeds the electrode size, the current approaches a steady state, and sigmoidal voltammograms will be observed. Figures 4(a) and 4(b) show the sigmoidal behavior of cyclic voltammogram at the diamond electrode for a redox kinetics of ferro-ferricyanide. In contrast, planar diffusion dominates at small values of $(Dt)^{1/2}/r^2$ and peaking was observed. Hence, depending on the timescale of the experiment (at various scan rates), the same electrode may exhibit a peak-shaped or sigmoidal voltammogram. Figures 4(c) to 4(k) show peak-shaped voltammograms for electrodes of the same area, where the scan rate was increased from 25 mV/s to 20,000 mV/s. The figures indicate that planar diffusion dominates and the

electrode size is larger than the diffusion layer thickness. A similar phenomenon has been observed for ultramicrometallic electrodes.[19] We have observed similar behavior for the diamond electrode. The change from semi-infinite planar diffusion to semi-infinite hemispherical diffusion may be achieved by either decreasing the electrode dimensions, by performing voltammetry at a constant scan rate, or by performing voltammetry at various scan rates, using a fixed electrode size. The number of electrons that transferred during the redox reaction is one; this can be determined from the separation between the peak potentials in the cyclic voltammogram. Figure 4 shows that the ΔE_p values are significantly higher than the predicted value of 59 mV for a one electron-transfer reaction. This indicates the occurrence of slow electron-transfer kinetics at the diamond electrode surface. "Electrochemical irreversibility" has caused the peak separation, ΔE_p, to increase. The high value of peak separation could also be due to the high resistivity of diamond film grown by CVD processes.[12,13]

It is possible to study redox kinetics in high resistivity solutions using microelectrodes. The double-layer capacitance at the diamond microelectrode will be significantly reduced as the electrode size is decreased. This will result in a small RC time constant which is proportional to the electrode size. The small RC time constant allows high-speed voltammetric experiments to be performed at the microsecond timescale, as well as scan rates higher than 10^6 V/s; hence it is possible to investigate the kinetics of very fast electron-transfer reactions. The rate of mass transport to and from the electrode increases as the electrode size decreases. As a consequence of the increase in mass-transport rates and the decrease in charging currents, microelectrodes exhibit excellent signal-to-background characteristics in comparison to their large counterparts. We have observed very low double-layer capacitance (10 μF/cm^2 – 1 pF/cm^2) at the macrodiamond electrode (area: 0.7122 cm^2); consequently, there is an increase in the signal-to-noise ratio. We have further reduced the electrode size to 0.003 cm^2, which will certainly aid in reducing the double-layer capacitance and enhancing the signal-to-background ratio further. The very low corrosion rate of diamond, low double-layer capacitance, ease of preparation of the microdiamond electrode, and minimum contamination of the ambient could enable its use in bioelectroanalytical microsensor applications.

4. Conclusions

We have demonstrated for the first time the evaluation of fabricated submillimeter diamond electrode using cyclic voltammetry. The redox kinetic behavior of ferro-ferricyanide has been investigated at the diamond electrode. Planar and hemispherical diffusion towards the diamond electrode has been demonstrated using slow scan (sigmoidal curve) to fast scan cyclic voltammetry (peak-shaped curve). Finally, we have shown that the diamond electrode could be used to study redox kinetic behavior. Therefore, we anticipate that the diamond electrode may have significant uses in biosensor applications. To validate this statement, it is necessary to investigate other redox species for their kinetic behavior in a suitable electrolyte solution. The electrode size which we used in this study was 42 times smaller than the electrode size employed in ref. (6). Slow and fast scan cyclic

voltammetry was used to investigate the redox kinetics and the change in diffusion mechanism of the species at the submillimeter diamond electrode/solution interface which is totally new in this study. Only slow scan voltammetry was used in ref. (6) to study the redox kinetics at the diamond electrode.

We have reported the growth of boron-doped diamond on a molybdenum substrate by the microwave plasma CVD process using hydrogen with methane as a carbon source. Background cyclic voltammograms for diamond electrode showed that the electrode was stable over a wide potential range in 0.5 M NaCl as the supporting electrolyte. The background current observed for the diamond electrode is in the nanoampere range. To our knowledge, this is the first report on the evaluation of background current at the diamond electrode. It may be qualitatively concluded, based on the stability characteristics observed in background cyclic voltammetry studies, that diamond electrodes have significant applications in electroanalytical chemistry. We have investigated the redox kinetics of ferro-ferricyanide at the diamond electrode and the peak separation was observed to be in the range of 1,000 mV at a scan rate of 100 mV/s. This indicates the electrochemical irreversibility or slow electron-transfer kinetics at the diamond/solution interface.

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