Investigation of Electro-Oxidation of Methanol and Benzyl Alcohol at Boron-Doped Diamond Electrode: Evidence for the Mechanism for Fouling Film Formation

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Boron-doped diamond (BDD) and glassy carbon (GC) electrodes are compared for electrochemical oxidation of methanol and benzyl alcohol. Cyclic voltammograms reveal that BDD electrode produces good oxidation signals for both methanol and benzyl alcohol, while GC produces no significant oxidation signal for either methanol or benzyl alcohol. Amperometric measurement of oxidation of methanol and benzyl alcohol on BDD shows development of a fouling film for benzyl alcohol but not for methanol. Prolonged (24 h) polarization of the BDD electrode at +2.0 V in benzyl alcohol generated enough fouling film for investigation by AFM, SEM, Raman, and FTIR techniques. AFM and SEM microscopy images confirm a fouling film confined to the low-lying regions of the polycrystallite BDD surface, indicating that the active sites of benzyl alcohol oxidation are located within these low-lying regions. The fouling material generated in the process of benzyl alcohol oxidation was identified from Raman and FTIR spectroscopy as polyester. Experiments confirm the fouling film can be removed and the electrode surface reactivated by brief polarization at +3.0 V. Amperometric results of concentration dependence confirm the BDD electrode is well suited for quantitative analysis applications of methanol and benzyl alcohol, with recognizable oxidation currents at micromolar concentration levels.

1. Introduction

Organic pollutants in wastewater are an issue of increasing concern as global industrial development continues.[1] Methanol and benzyl alcohol are among the organic pollutants commonly found since both are organic solvents with extensive application in the manufacture of colors, dyes, drugs, perfumes, degreasing agents, fuel additives, and so forth. Methanol and benzyl alcohol are now common contaminants in food and have become a matter of significant concern since both chemicals are highly toxic and frequently fatal to human beings. As a result, the biomedical, chemical, drug, and food industries are greatly interested in highly sensitive and selective organic sensors and improved methods of wastewater treatment. Electrochemical technology is often applied in senor applications and is becoming a new alternative for efficient and cost-effective wastewater treatment. For reaction with target materials in these applications, it is common to construct anodes from glassy carbon or the oxides of gold, platinum, or composite metals.[2–4] However, surface adsorption and fouling of the electrode by accumulated target substance or reaction product can place severe limits on electrode utility. Therefore, efficient, stable, refreshable, and environmentally friendly anode materials are required.

Boron-doped diamond (BDD) thin films fabricated by chemical vapor deposition (CVD) techniques have attracted interest as electrode material due to good physical and electronic properties with respect to hardness, chemical inertness, thermal conductivity, and electrical conductivity.[5,6] For example, BDD electrodes exhibit a wide working potential in aqueous electrolytes with low and stable voltammetric background current, low and weak adsorption of polar molecules, and high stability under strongly oxidizing conditions.[7,8] The superiorities of BDD relative to other materials is motivating the use of BDD electrodes in electroanalytic applications and also is stimulating investigation into uses such as wastewater purification.

A number of reports have investigated the electrochemical oxidation of organic pollutants such as phenol and complex agents related to wastewater treatment by the use of BDD electrodes.[9–13] Recently, Comninells et al. observed that the electro-oxidation process of aromatic compounds on a BDD electrode resulted in electrode fouling due to the formation of polymeric film on the electrode surface,[9–11] inhibiting extended use of the electrode. However, because the mechanism of the polymeric film generation is still not well characterized, it is desirable to develop a fundamental understanding of the electro-generation and removal of polymeric films on BDD electrodes.

To this end, this paper reports the use of a BDD electrode for electrochemical oxidation of methanol and benzyl alcohol in K_2SO_4 solution by cyclic voltammetry (CV) and amperometry. Polymeric film formation for benzyl alcohol is found. The fouling film on the BDD surface is characterized by AFM, SEM, Raman, and FTIR techniques. Fast and simple removal of the fouling film by anodic polarization is confirmed.

2. Experimental Section

BDD electrocatalytic behavior was investigated by cyclic voltammetric and amperometric techniques in a standard three-

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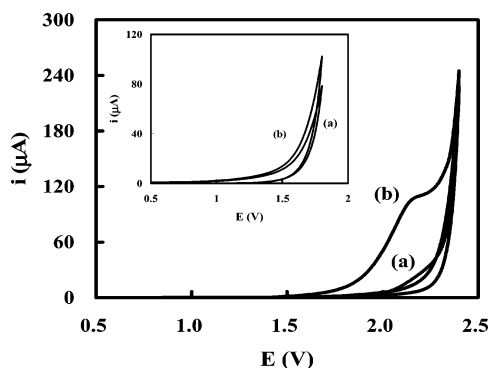|| Center for Micro/Nano Technology Research, National Cheng Kung University.

Electro-Oxidation at Boron-Doped Diamond Electrode

J. Phys. Chem. B, Vol. 110, No. 39, 2006 **19427**

Figure 1. Cyclic voltammograms for BDD electrode in 0.5 M K_2SO_4 solution in the absence (a) and presence (b) of 1 mM methanol at a scan rate of 20 mV s^{-1}. Inset figure for GC electrode at the same condition.
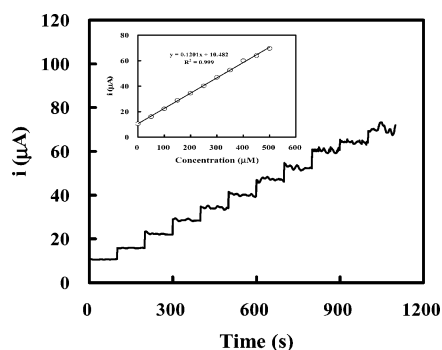

Figure 2. Typical amperometric response of the BDD electrode to step-by-step injection of methanol in 0.5 M K_2SO_4 (at constant potential 2.3 V). Inset figure shows linear calibration plot of response current against methanol concentration.

electrode configuration. For the working electrode, BDD thin films were grown by CVD on a single side of a silicon (Si) substrate material (Diachem Condias, Germany) and used with a Ag/AgCl reference electrode. Platinum wire was the counter electrode. The BDD electrode with no surface pretreatment was held in a Teflon mounting. For comparison, a commercial glassy carbon (GC) electrode (Bioanalytical Systems) was used. The GC electrode was polished with 0.3 and 0.05 μm alumina−water suspensions followed by rinsing with high-purity water. Electrochemical measurements were recorded by an Autolab electrochemical analyzer (Autolab PGSTAT30, ECO Chemie). All reagents were of the highest available grade from Merck and used without further purification. All solutions and subsequent dilutions were prepared using deionized water which was passed through a Millipore ultrapurification system. All experiments were controlled at 25 °C (with an accuracy of 0.05 °C) using a water thermostat (HAAKE D8 and G).

The BDD and GC electrodes were first tested by CV in 0.5 M K_2SO_4 solution with and without methanol or benzyl alcohol. The BDD electrode was then tested by amperometry in the solution with methanol or benzyl alcohol. Next the BDD electrode was subjected to 24 h of polarizing in 0.5 M K_2SO_4 with 80 mM benzyl alcohol at +2.0 V in order to induce a substantial fouling film sample. Surface morphology of the BDD electrode in its initial state and after 24 h polarization was measured in the air with an atomic force microscope (AFM) (Solver L7S, NT-MDT Co., Russia). A gold-coated Si$_3$N$_4$ tip (NT-MDT Co., Russia) was used in the contact mode. Surface morphology was also investigated by scanning electron microscopy (SEM) (JEOL JSM 35) operating at 20 keV.

Micro-Raman scattering study of the electrode was performed by a confocal RENISHAW micro-Raman system (RENISHAW
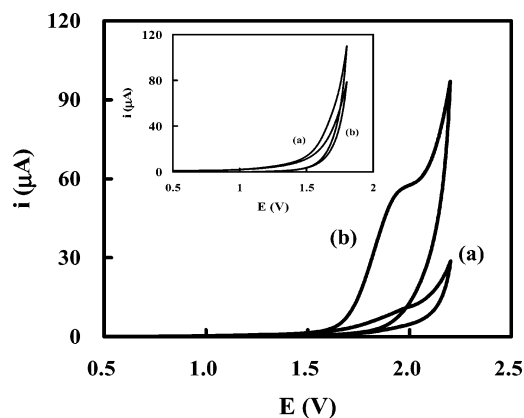

Figure 3. Cyclic voltammograms for the BDD electrode in 0.5 M K_2SO_4 solution in the absence (a) and presence (b) of 1 mM benzyl alcohol at a scan rate of 20 mV s^{-1}. Inset figure for the GC electrode at the same condition.
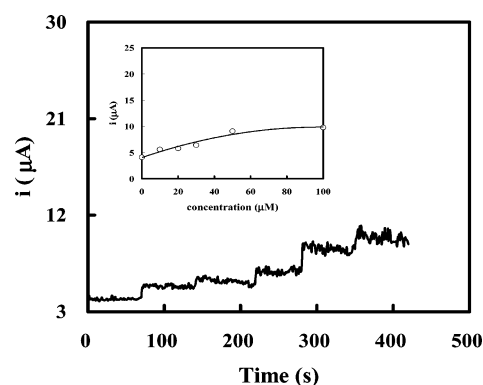

Figure 4. Typical amperometric response of the BDD electrode to step-by-step injection of benzyl alcohol in 0.5 M K_2SO_4 (at constant potential 2.0 V). Inserted figure shows relation of plot response current to benzyl alcohol concentration.

System 1000, Renishaw plc., Gloucestershire, U.K.) with the spectrometer equipped with an 1800-lines/mm grating. Raman spectra were recorded from the diamond top surface using a 20× objective to focus and correct the scattered laser light. The excitation source was a 633 nm helium neon laser with a power of 17 mW. Data were calibrated with the silicon band at 520 cm^{-1}. Raman spectra were collected using a 10 s exposure time and 5 accumulations. Raman maps were scanned in 3 μm steps. All Raman spectral data were processed with the software supplied by RENISHAW, and background corrections were made as needed. FTIR spectra were recorded by a Nicolet Nexus 470 Fourier transform spectrometer (4 cm^{-1} resolution), and the angle of incidence from the normal is 0°.

3. Results and Discussion

3.1. Electrochemical Analysis. *3.1.1. Electro-Oxidation of Methanol via CV.* Figure 1 shows the CV plots for the BDD electrode in 0.5 M K_2SO_4 with and without 1 mM methanol, with an inset figure of the GC electrode with and without methanol for easy comparison. Electro-oxidation of methanol using the BDD electrode produced a distinct oxidation peak at +2.3 V (versus the Ag/AgCl reference electrode). On the other hand, the inset GC electrode figure shows approximately identical curves with and without methanol, i.e., no oxidative response for methanol. It is clear, then, that the BDD electrode is a sensitive detector of methanol, while GC is of no use for this function.

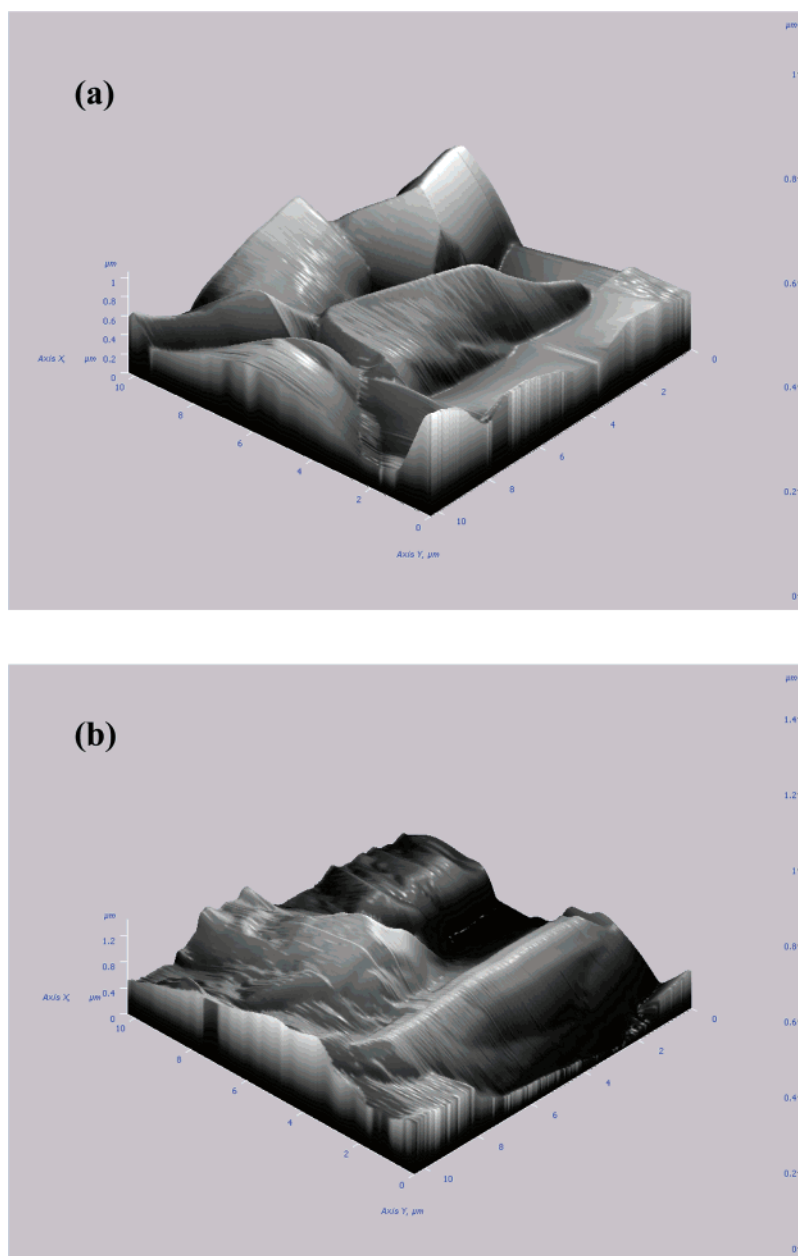*3.1.2. Electro-Oxidation of Methanol via Amperometry.* Figure 2 shows the amperometric results for BDD in 0.5 M

Figure 5. AFM image of the BDD electrode morphology of (a) the as-produced unfouled BDD and (b) the same BDD electrode in 0.5 M K_2SO_4 with 80 mM benzyl alcohol at 2.0 V for 24 h polarization.

K_2SO_4 solution with various methanol concentrations. This gives us a picture of the response current over time and the sensitivity of the system to concentration. Amperometric results are especially useful for determining whether the electrode is developing a reaction-inhibiting fouling film. Inspection of Figure 2 shows that the noise level at each step is small, the noise increase per step is small, and the slope of average current of each step is approximately zero. Also, the relation between current and concentration (inset figure) is linear. Taken together, these indicate that there is no fouling film when methanol is oxidized on BDD under the conditions of the experiment. It can also be seen that the BDD electrode remains sensitive to methanol, even at the minimum concentration, emphasizing the utility of BDD for sensitive methanol sensor devices.

3.1.3. Electro-Oxidation of Benzyl Alcohol via CV. Figure 3 shows the CV plots with and without 1 mM benzyl alcohol for the BDD and GC electrodes. A clearly defined oxidation peak for the BDD electrode with respect to the background signal was obtained at +2.0 V versus Ag/AgCl. The inset figure of Figure 3, the GC electrode with and without benzyl alcohol, shows oxidation and background curves that are approximately the same, i.e., no oxidative response. Clearly, the BDD electrode has a sensitive response to benzyl alcohol while the GC response to benzyl alcohol is negligible.

3.1.4. Electro-Oxidation of Benzyl Alcohol via Amperometry. Figure 4 shows the amperometric results for BDD in 0.5 M K_2SO_4 solution with various benzyl alcohol concentrations, with an inset figure showing the current/concentration relation. Inspection of this figure shows benzyl alcohol has very different pattern than the pattern for methanol in Figure 2. However, it should be noted that the *y*-axis (μA) scales of Figures 4 and 2 are very different, so the noise levels cannot be directly compared. Figure 4 details the amperometric response for the clean un-pretreated BDD electrode in 0.5 M K_2SO_4 at +2.0 V with subsequent step-by-step additions of benzyl alcohol. Although the response current increases with increasing benzyl alcohol
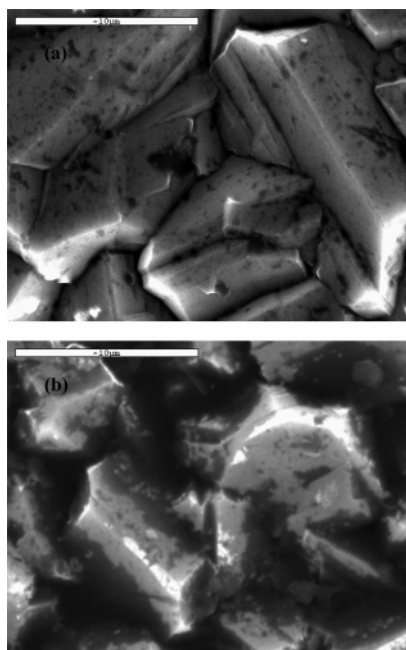
Electro-Oxidation at Boron-Doped Diamond Electrode

J. Phys. Chem. B, Vol. 110, No. 39, 2006 **19429**

Figure 6. SEM image of the BDD electrode surface of (a) the as-produced unfouled BDD and (b) the same BDD electrode in 0.5 M K_2SO_4 with 80 mM benzyl alcohol at 2.0 V for 24 h polarization.

concentration, the relation between response current and benzyl alcohol concentration is not linear (shown as the inset figure). Further, the noise becomes larger with increasing benzyl alcohol concentration. Additionally, the slope of the average current per step decreases. All of these factors indicate possible fouling of the electrode.

Comninellis et al.[9,10] reported electrochemical oxidation of aromatic organic compounds such as phenol and 2-naphthol at BDD electrodes, and in these experiments they observed that the response current declined as the oxidation time increased. Therefore, they reported deposition of the polymeric film on the BDD electrode surface during oxidation, indicating that the film accumulation was reducing the number of available active sites on the electrode surface. As will be seen below, we observed a similar film after benzyl alcohol oxidation at the BDD electrode in our test system.

3.2. Fouling Film Analysis. To optimize the electrochemical reaction of benzyl alcohol at the BDD electrode, it is essential to investigate the fouling film. We investigated this by comparing the as-produced BDD electrode with the same electrode after 24 h of +2.0 V polarization in benzyl alcohol, as described above, i.e., after a significant fouling film had been deposited.

3.2.1. AFM Analysis. A 10 μm $\times$ 10 μm AFM image of the surface of the as-produced unfouled BDD film (on silicon substrate) is shown in Figure 5a. The figure reveals that the diamond film is continuous over the entire scanned area, showing distinct polycrystalline morphology and sharp, well-faceted microcrystallites of a few micrometers in width. The BDD film is composed of many twinned randomly oriented crystallites with clearly defined grain boundaries. In comparison, Figure 5b shows an AFM image of the same BDD electrode (different location from Figure 5a) after 24 h polarization in 0.5 M K_2SO_4 with 80 mM benzyl alcohol (as described above). Clearly, the characteristic surface morphology of the electrode has changed. Prepolarization AFM imaging reveals distinct crystallites and facets, but the postpolarization image of Figure 5b reveals a surface that is devoid of crystalline characteristics and instead seems composed of laterally grained (an artifact of the AFM scanning methodology) rounded hillocks.
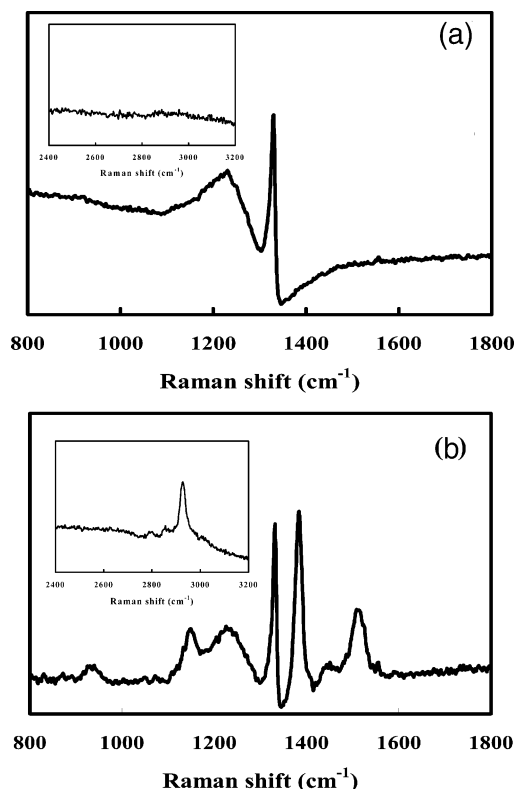

Figure 7. Raman spectra of the boron-doped diamond thin film of (a) the as-produced unfouled BDD and (b) the same BDD electrode in 0.5 M K_2SO_4 with 80 mM benzyl alcohol at 2.0 V for 24 h polarization.

3.2.2. SEM Analysis. Figure 6a shows a typical SEM image of the as-produced BDD surface. Similar to the AFM image of Figure 5a, clearly defined twinned crystallites with distinct faceting and random orientation can be observed. The bright and dark features on the crystallites are believed to be regions of different electron affinity. Figure 6b shows the SEM image of the same BDD electrode after 24 h +2.0 V polarizing in 0.5 M K_2SO_4 and 80 mM benzyl alcohol (as above). Examination of Figure 6b reveals dark material filling the low-lying regions between the diamond crystallites. Although the rounded hillocks revealed in the Figure 5b AFM image could be interpreted as erosion of the crystallite surface, the SEM image of Figure 6b strongly suggests material deposition. The AFM and SEM data together with knowledge of the conditions and materials of the experiment strongly suggest deposition of a fouling film on the BDD electrode surface. However, it is essential to confirm this interpretation and, if correct, to analyze the material of the fouling film.

3.2.3. Raman and FTIR Spectroscopic Analysis. We employed Raman spectroscopy for the next phase of our investigation. Figure 7a displays the Raman spectrogram of the BDD film before the 24 h polarizing treatment (as above) and shows a sharp peak at approximately 1334 cm^{-1}, a well-known characteristic of crystalline diamond. A broad peak centered at approximately 1200 cm^{-1} is also observed and possibly is Fano-type asymmetry of the 1334 cm^{-1} peak or, alternately, may be associated with photoluminescence.[14−16] In Figure 7b, the Raman spectrogram of the BDD film after polarizing is clearly much different than before polarizing (Figure 7a). The diamond peak at 1334 cm^{-1} can still be seen, but the additional peaks are clear evidence of additional material on the BDD electrode surface, presumably generated during benzyl alcohol oxidation. The band at approximately 1150 cm^{-1} in Figure 7b indicates C−phenyl vibration.[17,18] The band at 2920 cm^{-1} is a C−H
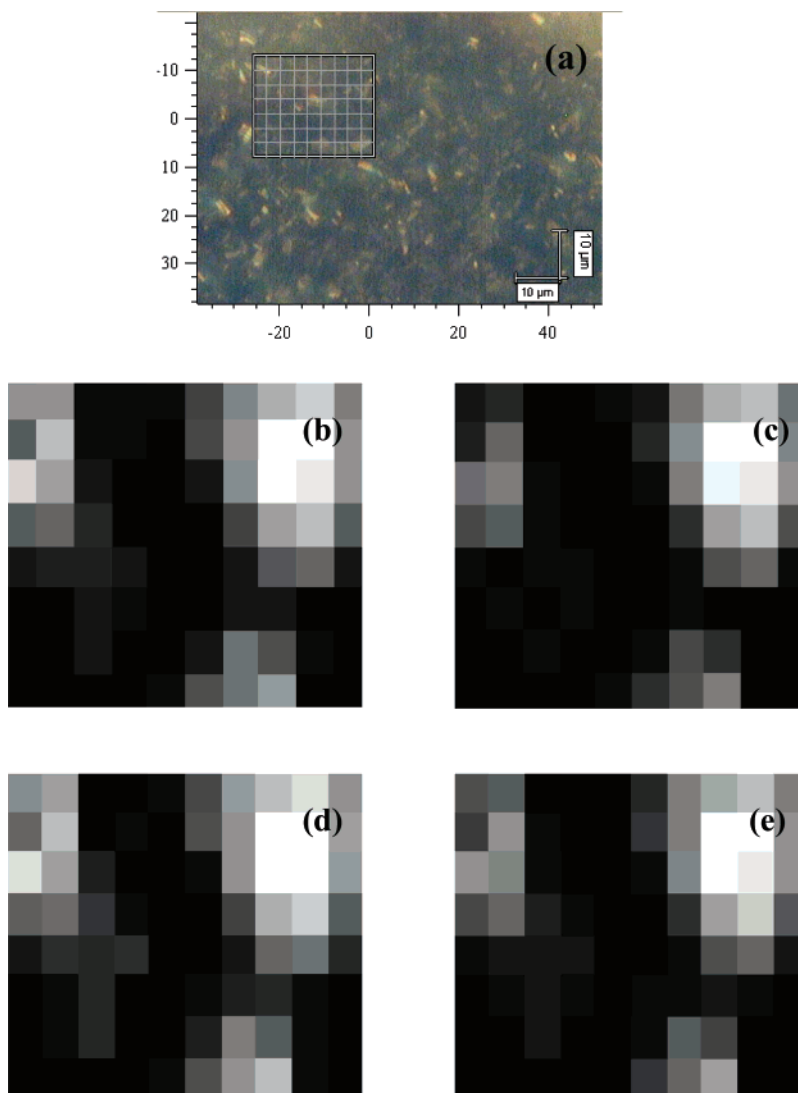
Figure 8. The BDD electrode in 0.5 M K$_2$SO$_4$ solution with 80 mM benzyl alcohol at 2.0 V for 24 h polarization: (a) optical microscopy; Raman mapping at linear intensity (b) 1150, (c) 1380, (d) 1450, and (e) 1500 cm^{-1} for the gridded areas in the respective optical micrographs. In Raman maps, white corresponds to high Raman intensity whereas black corresponds to no Raman intensity.

stretching vibration, and the band at 1500 cm^{-1} can be considered evidence of a benzene ring.[17−19] The sharp peak at 1380 cm^{-1} is interpreted as the ester mode.[20] With knowledge that the reactants include only H$_2$O, K$_2$SO$_4$, and benzyl alcohol, we can therefore assume that the film is one or more types of polyester with the benzene rings joined by C−C phenyl links. Further support for the polyester model can be drawn from the fact that while oxidation of benzyl alcohol showed a strong tendency toward fouling, the same system oxidizing the similar but nonaromatic organics as methanol showed zero fouling film. Moreover, the peak at approximately 1450 cm^{-1} can be interpreted as carboxylates, and the peak at approximately 950 cm^{-1} can be interpreted as a carbonyl bond. These two signals both indicate the formation of polyester at the BDD electrode in the process of benzyl alcohol oxidation.[19,21]

The Raman map in Figure 8 was acquired by analyzing the peak intensity at 1150 (C−phenyl vibration), 1380 (approximately the ester), 1450 (carboxylate), and 1500 (benzene ring) cm^{-1}. The white regions correspond to high Raman intensity whereas the black regions correspond to zero Raman intensity. Each square in the Raman map represents a 3 μm × 3 μm area. Inspection of Figure 8 shows the peak intensity varies widely and indicates the fouling film is not homogeneous. Figures 6 and 8 are from different locations of the film-fouled BDD

electrode. These figures have moderately different total areas but are similar enough in size that the figures can be compared for average characteristics. Comparison of the Figure 6b SEM micrograph and the Figure 8 Raman map shows that both representations of the film-fouled surface contain mixed light and dark regions of similar size and distribution. The above data reasonably confirm the premise that the fouling film is found only in the low-lying regions between the diamond crystallites and the peaks of the crystallites protrude from the film. Because we know that Figure 6b is less reactive than Figure 6a and the only difference between the figures is the film-covered regions, then the regions covered by the film can be assumed to be the active sites of the BDD electrode surface.

FTIR analysis is employed to cross-check the fouling material on the BDD electrode surface, and the results are shown in Figure 9. In comparison with the spectra of the BDD electrode without any pretreatment as Figure 9a, Figure 9b can be observed a significant adsorption band for ester (2900−3100 cm^{-1}) from the spectra of the BDD electrode surface after 24 h polarization at 2.0 V in 80 mM benzyl alcohol solution. Taken together with Raman and FTIR spectral results, it can indicate the formation of polyester in the process of benzyl alcohol oxidation on the BDD electrode surface.
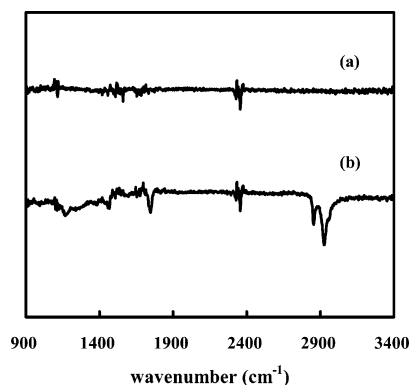
Electro-Oxidation at Boron-Doped Diamond Electrode

*J. Phys. Chem. B, Vol. 110, No. 39, 2006* **19431**

Figure 9. FTIR spectra of the BDD electrode of (a) the as-produced unfouled BDD film and (b) the same BDD electrode in 0.5 M K_2SO_4 with 80 mM benzyl alcohol at 2.0 V for 24 h polarization.

3.3. Mechanism for Fouling Film Formation. On the basis of the Raman and FTIR results, the following reaction mechanism is proposed for the anodic oxidation of benzyl alcohol in this investigation. First, benzyl alcohol is oxidized to benzoic acid or free radical, as showed in eqs 1−3. Second, as the result of dehydration, ester is generated by the combination of benzyl alcohol and benzoic acid (as showed in eq 4). Furthermore, the formation of polymeric film is caused by the combination of benzene rings due to free radical attack.
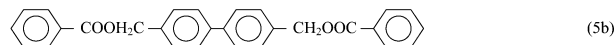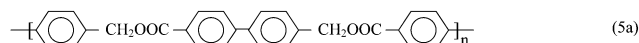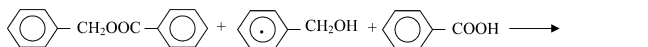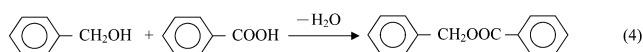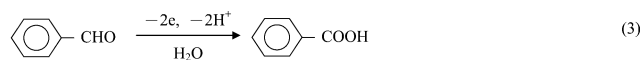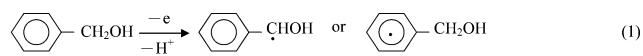
However, it is a random attack caused by free radicals, and the materials of polymeric film are not homogeneous. The polymeric film may consist of materials 5a, 5b, and so forth. Although the materials of polymeric film are uncertain, material 5a still can be confirmed as the major product of the polymeric film for prolonged polymerization. Other materials, such as material 5b, will be minor product or even scarce in the deposited film because of their solubility or small molecular weight.

3.4. Electrode Refresh. It is desired to remove the fouling film and refresh the BDD electrode so as to retain electrode activity for prolonged use. This is especially important for high-volume applications such as wastewater treatment.

In the literature, the most common method for removing a fouling film is applying a high potential to the electrode in order to generate powerful oxidants such as hydroxyl radicals.[9−11,22] So we took a clean BDD electrode and set up the initial conditions used in our fouling experiment, i.e., polarizing at +2.0 V
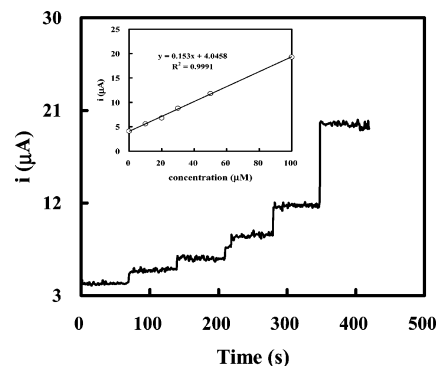

Figure 10. Typical amperomertic response of the BDD electrode to step-by-step injection of benzyl alcohol in 0.5 M K_2SO_4 for 70 s at +2.0 V and 30 s at +3.0 V. Inserted figure shows linear calibration plot of response current against benzyl alcohol concentration.

in 0.5 M K_2SO_4 solution. Then, with the potential set at +2.0 V (versus Ag/AgCl), we injected benzyl alcohol and recorded the oxidation current. This condition was maintained for 70 s, after which the potential was raised to +3.0 V and maintained for 30 s. At the end of 30 s, the potential was returned to +2.0 V, and benzyl alcohol was injected again. The results can be seen in Figure 10. A similar experiment with stepwise benzyl alcohol increments but constant +2.0 V potential was shown in Figure 2, wherein the results indicated film formation. In contrast, Figure 10 shows no film formation since the noise per step remains constant, the slope of current per step is approximately zero, and the inset figure current/concentration curve (from 10 to 100 μM ($R^2 = 0.999$)) is linear. In other words, the data indicate that intermittent +3.0 V treatment removed the fouling film and the electrode retained its full electrochemical activity.

Additional confirmation of the fouled diamond film after polarization at +3.0 V was obtained from the Raman spectrum (not shown here), which was consistently similar to that shown in Figure 5a, i.e., the Raman spectra all show a clean diamond surface. Therefore, the presented method for refreshing the BDD electrode surface is effective and easily implemented, thereby allowing continued detection or wastewater treatment of benzyl alcohol.

4. Conclusion

Boron-doped diamond (BDD) and glassy carbon (GC) electrodes have been compared for electrochemical oxidation of methanol and benzyl alcohol. Cyclic voltammetry showed BDD produces good oxidation signals for both methanol and benzyl alcohol, while GC produces no significant oxidation signal for either methanol or benzyl alcohol. Amperometric measurement on BDD showed a fouling film developed for benzyl alcohol but not for methanol. Polarization of the BDD electrode for 24 h at +2.0 V in benzyl alcohol generated enough fouling film for investigation by AFM, SEM, Raman, and FTIR techniques. AFM and SEM microscopy images confirmed a fouling film confined to the low-lying regions of the polycrystallite BDD surface and indicated that the active sites of benzyl alcohol oxidation are located within these low-lying regions. The fouling material was identified as polyester from Raman and FTIR spectroscopy. Experiments confirmed the fouling film can be removed and the electrode reactivated by brief polarization at +3.0 V. Amperometric results of concentration dependence confirmed the BDD electrode is well suited for quantitative analysis applications of methanol and benzyl alcohol, with recognizable oxidation currents at micromolar concentrations. The characteristic of good sensitivity for the BDD

Chang et al.

electrode is valuable for the electroanalysis of methanol and other alcohols.

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