

Detection of Ascorbic Acid in an Ethanol–Water Mixed Solution on a Conductive Diamond Electrode

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Conductive boron-doped diamond thin-film electrodes have been shown to be highly suitable as electrochemical detectors in flow injection analysis (FIA) due to the lack of electrode deactivation due to fouling and the ability to withstand highly positive electrochemical potentials. In the present work, a diamond electrode was applied to the detection of ascorbic acid (AA) in an alcohol–water mixed solution. During FIA of AA in an ethanol (EtOH)–water solution including 0.1 M $NaClO_4$, the interference from EtOH oxidation that would have been observed with a Pt electrode was avoided, and the amperometric response for AA was observed with the use of a conductive diamond as the electrode material. Moreover, The detection limit for AA that could be observed was lower than that for a glassy carbon electrode, because diamond exhibits a lower background current, smaller background noise, and smaller injection noise. These findings suggest that the diamond electrode may be applied in the detection of other redox-active impurities and added substances in alcohol or alcohol–water solutions, such as chlorophyll, nicotinamide, caffeine, riboflavin, and *dl*-α-tocopherol.

Diamond is a good insulator, with a resistivity higher than 10^{13} Ω cm. However, boron-doping during CVD synthesis produces conductive films with low resistivity, ranging from 10–10^{-3} Ω cm.[1] For use as an electrode for electrochemistry, conductive diamond is superior to conventional electrode materials, because it possesses excellent characteristics, such as a wide electrochemical potential window in aqueous media,[2,3] low background current,[4] negligible corrosion, and fast electron transfer kinetics for outer-sphere redox species.[4–6]

Recently there has been an increasing interest in studying the potential for application of diamond films, covering an extremely wide range of fields, including electronics, field emission displays, and sensors.[7] For the electroanalytical application, there has been an interest in further widening the field of applications through the use of surface modification.[8–14] In addition, diamond electrodes are attractive due to negligible adsorption of chemical species on the electrode surface.[15]

Specific recent electroanalytical applications of boron-doped diamond have included L-cysteine,[16] chlorophenols,[17] sulfur-containing compounds,[18] trace metals,[19] and carbamate pesticides.[20] The analytical performance has in every case been superior to that for glassy carbon (GC).[16–20] Thus, conductive diamond electrodes should be useful for the electroanalytical investigation of various chemical substances.

However, no example exists of conductive diamond being used for the detection of chemical substances in aqueous media containing alcohols, to the best of our knowledge. It has been shown that unmodified diamond electrodes are remarkably insensitive to various alcohols,[21] in contrast to Pt. Thus, the aim of the present study was to investigate whether or not the diamond electrode is appropriate for such analysis, especially detecting and assaying impurities and added substances in *alcohol–water mixtures*. In this work, ascorbic acid (AA) was chosen as the analyte.

AA is included in many foods (such as vegetables, fruits, and green teas), beverages (containing ca. 0.02–0.04% AA) made from natural or artificial juices, dairy products (containing ca. 0.005–0.01% AA), and liquors (such as beers, wines, and cocktails) (containing ca. 0.003% AA). AA is added as an oxidation inhibitor and as one of several vitamins to improve one's health. In the present study, we have as one of our objectives the analysis of AA in ethanol (EtOH)–water mixed solutions with compositions similar to commercial liquors. In the quality control of foods, this work has significance. The detection of AA in foods is generally performed using a UV detector coupled with high-performance liquid chromatography.[22] However, amperometric detection by means of an electrochemical reaction is generally more sensitive.[23,24]

For example, Cardwell and Christophersen carried out the determination of sulfur dioxide and AA in beverages using a flow injection analysis (FIA) system consisting of a dual channel electrochemical detector.[25] The dynamic range for AA was 17.0–284 μM, with a lower detection limit of approximately 9 μM.[25] This is superior to several tens of μM, which is the lowest quantification limit for previous UV detection methods. Granger et al. carried out the quantification of AA in an aqueous medium using a polycrystalline diamond electrode coupled with FIA and liquid chromatography.[26] As a result, the lower detection limit at the diamond electrode was 12 nM, while for a GC electrode, it was 4 times lower.[26] It was suggested that diamond exhibits as good or superior detector performance.[26]

The present study shows that AA can be detected in a mixed

alcohol-water solution with a diamond electrode, and therefore, diamond electrodes are expected to be useful in the detection and quantification of other types of added substances and impurities.

Experimental

Boron-doped diamond thin-films were prepared as deposits on *p*-Si (100) substrates (thickness: 0.65 mm) by use of a microwave plasma-assisted chemical vapor deposition instrument (MPCVD, Seki Technotron Corp., Tokyo, formerly ASTeX Corp., Woburn, MA). The boron source was B_2O_3 (extra pure grade, Wako Chemical Co.) dissolved in an acetone/methanol mixture (9/1, v/v) as the carbon source. The B/C atomic ratio was 10^4 ppm. Hydrogen was used as the carrier gas. The C/H ratio in the reaction gas was ca. 3%. The reaction pressure was 114 ± 1 Torr. The plasma output power was adjusted to 5 kW. Deposition was performed in the growth chamber for 10 h. The other CVD conditions have been detailed elsewhere.[27,28] The deposited films were highly crystalline, as evident from the strong characteristic peak at 1332 cm^{-1} in the Raman spectra of these films. In addition, a broad peak centered at ca. 1200 cm^{-1} was observed, which is characteristic of highly boron-doped samples. No additional peak due to sp^2 carbon was observed around 1500 cm^{-1}, indicating the high quality of these films. The thickness of the resulting diamond films was approximately 40 μm. A mirror-like polish was applied to the GC or Pt plate electrodes, with diamond paste (Fujimi, Inc.) and an alumina slurry (Büehler, Ltd.), respectively. Before the electrochemical measurements, the diamond, polished GC, and polished Pt plate electrodes were first rinsed with water and subsequently by acetone, last by methanol, and then air-dried. $NaClO_4$ (extra pure grade, Wako Chemical Co.) and AA (extra pure grade, Wako Chemical Co.) were used as received without further purification. Water was purified with a Milli-Q system (Millipore Co.). Its resistivity was over 17.3 MΩ cm. All other chemicals were of extra pure grade and were used without further purification. A freshly prepared AA aqueous solution was immediately stored on ice in darkness, and then this AA solution was used in all measurements at lower temperature (4 °C) in darkness, because of the spontaneous oxidation of AA to dehydroascorbate in light and at room temperature.

Figure 1 shows the time dependence of the transient current (corrected for the current using a blank solution) in FIA, when AA is added to the EtOH–water mixed solution ($x_{EtOH} = 0.4$, where x_{EtOH} is the mole fraction of EtOH vs water, with the $NaClO_4$ concentration being overall 0.1 M with respect to the volume of the mixture). This plot gives a slight decrease of the response current with time at lower temperature (4 °C) in darkness. However, degree of current-decreasing is more remarkable than that at room temperature on exposure to light. This fact suggests the necessity of the measurement at lower temperature in darkness to prevent AA from spontaneously oxidizing.

The measurements of the cyclic voltammograms (CVs) were made with an Ag/AgCl reference electrode (EE0081RE, Toa Electronics, Ltd.) and a Pt wire counter electrode. All of the potentials cited in this paper are referred to this reference electrode. The CVs were measured by use of an HSV-100 (HOKUTO DENKO Co.) potentiostat. The FIA measurements were carried out with a binary pump (PU611; GL Sciences, Inc.), an autosampler (Triathlon; Spark-Holland), a thin-layer flow-cell (GL Sciences, Inc.), and a data acquisition system (EZChrom Elite; Scientific Software, Inc.). The wall-jet-type flow-cell consisted of the Ag/AgCl reference electrode and a stainless steel tube (type 316) as the counter electrode. ED623 (GL Sciences, Inc.) and BAS LC-4C (Bioanalytical Systems, Inc.) units were used as the electrochemical detector in the FIA. The geometrical surface areas of the working electrodes used in the CVs and the FIA were 0.13 cm^2 and 0.55 cm^2, respectively. The potential sweep rate in each CV was 50 mV/s. The flow rate and sample injection volume in the FIA were 1 mL/min and 20 μL, respectively. The detailed procedure of the flow injection experiments has been reported previously.[29]

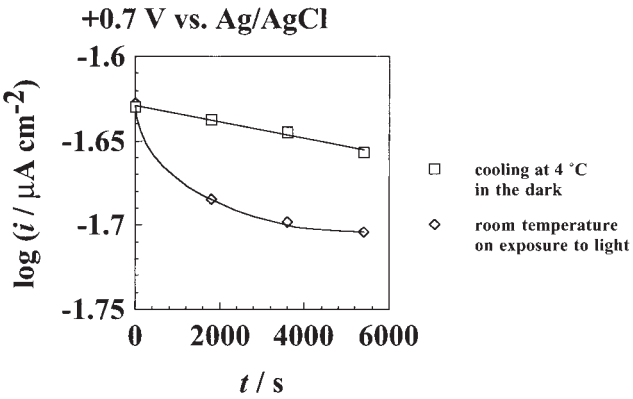

Fig. 1. Time dependence of the transient current (corrected for the current using a blank solution) in FIA, when AA is added to the solution at a constant detection potential (+0.7 V vs Ag/AgCl) for diamond electrode in EtOH–water mixed solution ($x_{EtOH} = 0.4$) containing 0.1 M $NaClO_4$ (sampling interval: 2 min; AA concentration: 500 nM).

Results and Discussion

The CVs for the various electrode materials in the ethanol-water mixed solution ($x_{EtOH} = 0.4$, where x_{EtOH} is the mole fraction of EtOH vs water, with the $NaClO_4$ concentration being overall 0.1 M with respect to the volume of the mixture) are shown in Fig. 2. The value, $x_{EtOH} = 0.4$, can be converted to 60% EtOH. Liquor containing 60% EtOH is rare, but this concentration of EtOH is the minimum value at which the onset of the current due to ethanol oxidation is clearly discernible when the GC electrode is used for the working electrode for CV in AA-free EtOH–water mixed solutions (not shown). On the contrary, when the diamond electrode was used as the working electrode for CV in an AA-free EtOH–water mixed solution, the CV behavior was very similar for all mole fractions of EtOH, with no clear peak or wave observed for ethanol oxidation (not shown). Therefore, it was expected that the diamond electrode would exhibit detector performance as good as or superior to that for GC, i.e., greater sensitivity and lower detection limits, at this mole fraction of EtOH. Thus, this value, $x_{EtOH} = 0.4$, was chosen. At the diamond electrode, negligible Faradaic current was observed in the potential range from +1.2 to −1.5 V vs Ag/AgCl. When the Pt electrode was used as the working electrode, an anodic peak at +0.8 V and a cathodic spike at +0.65 V were observed due to EtOH in the electrolyte solution. Thus, the Pt electrode is not appropriate to detect impurities in this solution. However, such responses were not observed for the diamond electrode

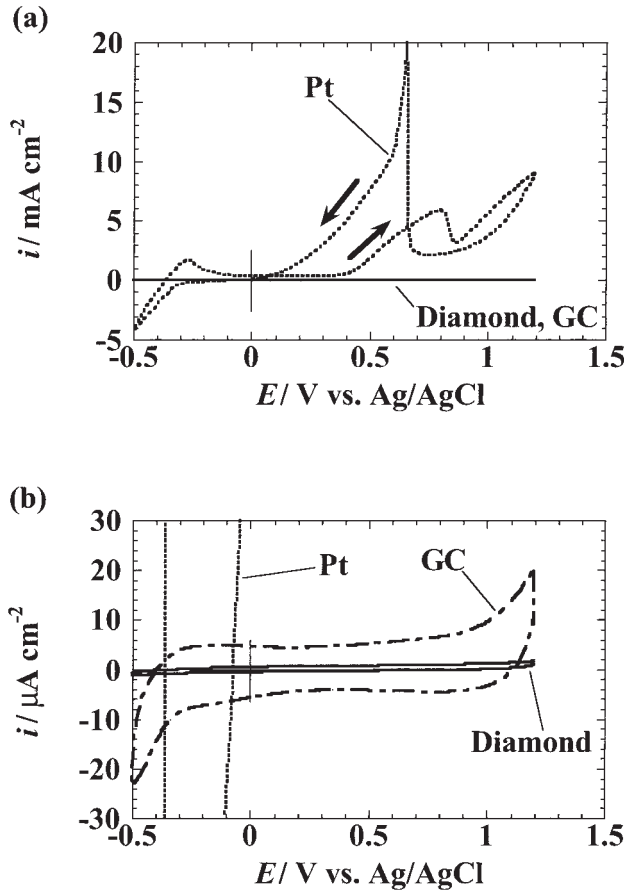

Fig. 2. (a) Typical CVs for various electrode materials (diamond, Pt, and GC) in EtOH–water mixed solution ($x_{EtOH} = 0.4$) containing 0.1 M $NaClO_4$ (potential sweep rate: 50 mV/s). The same CVs are shown in (b) at higher sensitivity.

as the working electrode. For the GC electrode, a reduction peak appeared around −0.3 V, and an onset of current due to oxidation was also observed around +0.8 V. On the contrary, at the diamond electrode, these responses were not observed. Moreover, because the background current of the diamond electrode was 0.95 μA/cm^2 (89% lower than that of the GC electrode, 8.7 μA/cm^2), it is expected that the diamond electrode should yield significantly greater sensitivity than the GC electrode. Also, because the potential window is 1.7 V, which is 1.6 times larger than that of the GC electrode, 1.1 V, the diamond electrode should be appropriate to detect a broader range of impurities in EtOH. The characteristic current response at the Pt electrode involves several different adsorbed species, including EtOH.[30,31] The latter is partially oxidized by a surface-catalyzed anodic dehydrogenation on Pt that is free of adsorbed oxygen or bulk oxide.[31] Based on the present knowledge of EtOH electrooxidation on Pt,[32–37] a general reaction scheme has been formulated that involves the following adsorbed species: water, EtOH, CO, acetaldehyde, and OH as well as other residues.[38] It is certain that the high catalytic activity for EtOH oxidation on Pt stems from its ability to adsorb various intermediates; conversely, the extremely low activity of diamond is due to its lack of ability to adsorb either reactants or intermediates.

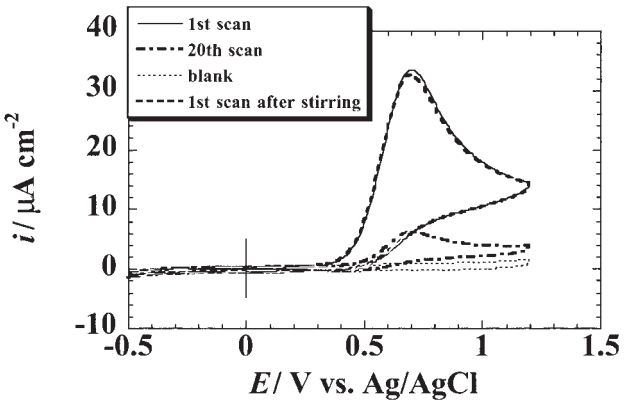

Fig. 3. CV of a diamond electrode in EtOH–water mixed solution ($x_{EtOH} = 0.4$) containing 0.1 M $NaClO_4$ + 1 mM AA (potential sweep rate: 50 mV/s).

The voltammetric response of a diamond electrode in an EtOH–water mixed solution ($x_{EtOH} = 0.4$) containing 0.1 M $NaClO_4$ and 1 mM AA is shown in Fig. 3. The shape and magnitude of the anodic peak, with the lack of a complementary reduction peak, is very similar to that observed in aqueous electrolytes and is consistent with a highly irreversible, overall two-electron process.[39] The anodic peak current due to AA oxidation was found to decrease with repeated potential sweeps, simply due to consumption of most of the AA in the vicinity of the diamond electrode. As shown, the response recovers fully after stirring.

In the FIA method, high sensitivity is expected, due to the efficient mass transport and absence of double-layer charging current. In addition, the absolute sensitivity is high, with the consumption volume of the sample solution on the order of several μL. Moreover, the low tendency of diamond to itself undergo anodic oxidation is expected to allow the background current to stabilize quickly after switching on the operating potential for amperometric detection. In FIA, since the hydrodynamic mass transport is caused by the solution flowing through a cell, the mobile phase carries electrogenerated product away from the electrode surface, depending on the flow rate.[40] This effect helps to minimize fouling and consequent deactivation of the electrode to a greater extent than found for a bulk-solution experiment such as CV.

Figures 4 and 5 compare the amperometric responses of diamond, GC, and Pt electrodes due to AA oxidation in the EtOH–water mixed solution ($x_{EtOH} = 0.4$) containing 0.1 M $NaClO_4$. The AA solutions that were injected were made up in the same EtOH–water mixed solution ($x_{EtOH} = 0.4$) containing 0.1 M $NaClO_4$. As discussed later in detail, the amperometric responses for AA oxidation at diamond and GC appear to be quite similar, while that for Pt was significantly poorer.

The background current at the Pt electrode was approximately 1200 nA/cm^2, roughly an order of magnitude higher than that observed at the diamond electrode (14 nA/cm^2) and also substantially higher than that observed at the GC electrode (50 nA/cm^2). This remarkably higher background current at the Pt electrode is due to EtOH oxidation. The relatively small background current for GC is due to a combination of EtOH oxidation and oxidation of the electrode itself. The magnitude of the AA responses at the various electrodes did not change

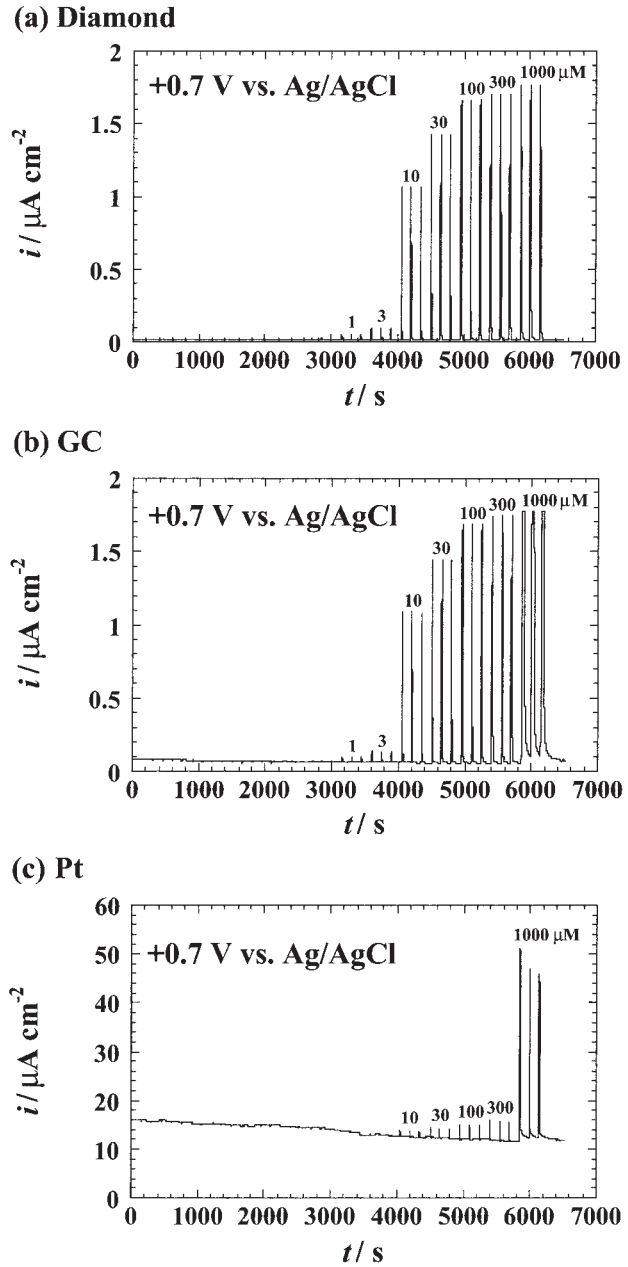

Fig. 4. Time dependence of the FIA current response when AA is added to the solution at a constant detection potential (+0.7 V vs Ag/AgCl) for (a) diamond, (b) GC, or (c) Pt electrodes in EtOH–water mixed solution ($x_{EtOH} = 0.4$) containing 0.1 M $NaClO_4$ (sampling interval: 2 min; AA concentration: 1 nM–1 mM).

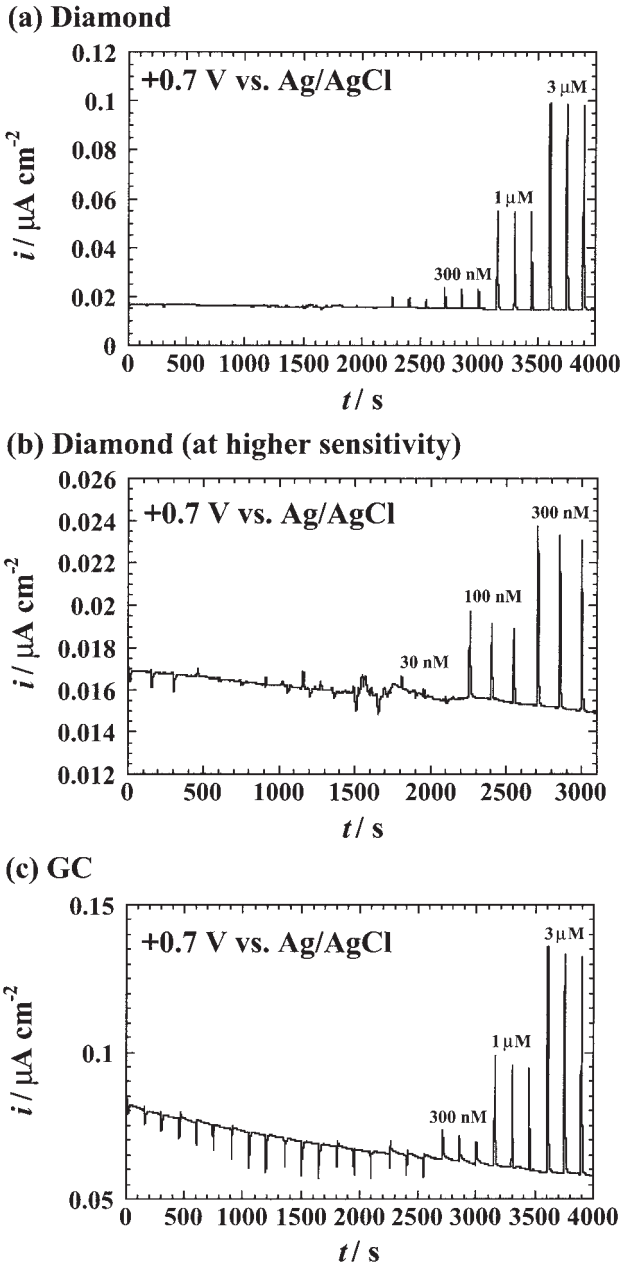

Fig. 5. The FIA current responses at higher sensitivity in Figs. 4a and 4b. The same FIA current response as (a) is shown in (b) at much higher sensitivity.

significantly, even when the order of the AA concentration in the injection solution was reversed, i.e., from higher concentration to lower concentration.

Based on the data in Figs. 4 and 5, the dependence of the transient current (corrected for the response using a blank solution) (i) versus the AA concentration ([AA]) is shown in Fig. 6. At the Pt electrode, a plot of $\log[AA]$ vs $\log i$ gave a straight line for the AA concentration range from 10 to 300 μM, but the slope of the plot was 0.33 rather than 1.0, which is an intrinsic difficulty in the determination of AA at Pt. The reason for this lack of sensitivity may be an overlapping of the AA response with that for EtOH oxidation in the solution. At the diamond and GC electrodes, because EtOH oxidation is inhibited compared to that for the Pt electrode, it is far more likely for a quantitative response to AA to be observed. For the higher AA concentration range (> 10 μM), the calibration curves shown in Fig. 6 were not fitted, perhaps because the injection of samples containing high AA concentrations led to a gradual poisoning of the electrode, leading to a decrease in sensitivity.

The results of Figs. 4, 5, and 6 are shown in Table 1. The sensitivities were estimated by fitting the log–log data (corrected transient current response vs AA concentration), with

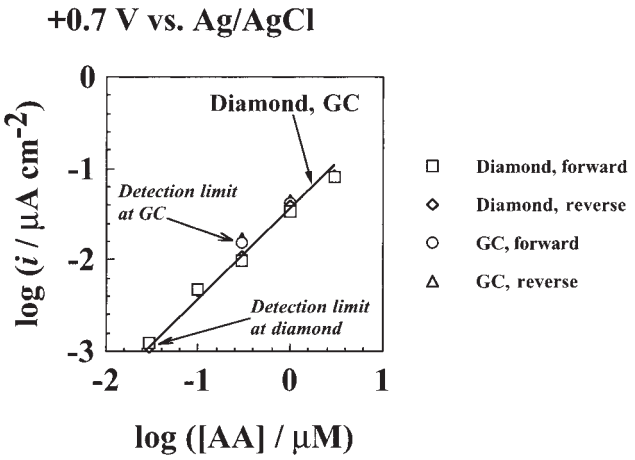

Fig. 6. Plots of the logarithm of the transient current (corrected for the response using a blank solution) versus the logarithm of the AA concentration in Fig. 4 (forward: injection in the order of increasing AA concentration; reverse: injection in the order of decreasing AA concentration). The detection potential was +0.7 V vs Ag/AgCl.

Table 1. Comparison of the Analytical Performance Characteristics for Diamond and GC Electrodes, Based on the Data in Figs. 4, 5, and 6[a)]

	Diamond	GC
Lower detection limit/nM	30	300
Sensitivity/nA μM^{-1}	21	21
Background current/nA cm^{-2}	14	50
Background noise/nA cm^{-2}	0.098	1.2
Injection noise/nA cm^{-2}	−0.55	−6.2

a) Detection potential: +0.7 V vs Ag/AgCl.

a slope of unity assumed. Here, the geometrical surface area of the working electrode is 0.55 cm^2. The noise of the background current was estimated from the amplitude of the fluctuations of the background current. The injection noise was estimated based on the transient current for an injected solution not containing added AA (background current subtracted). At the diamond electrode, the sensitivity was almost the same as that at the GC electrode. However, the lower detection limit at the diamond electrode was 10 times lower than that at the GC electrode. This result is slightly superior to that obtained in a purely aqueous solution by Granger et al.,[26] in which the lower detection limit at the diamond electrode was only 4 times lower than that at the GC electrode. Furthermore, the sensitivities obtained in the present work are superior (a factor of ca. 1.8 times lower) compared to those obtained in aqueous solution (ca. 12 nA/μM).[26] In the present work, the current responses ranging in the lower AA concentrations from 30 to 300 nM could not be obtained with the GC electrode because the background was larger current than that obtained with the diamond electrode. When an EtOH-free blank solution was injected, with an EtOH-free blank solution flowing, the magnitudes of the injection noise at the diamond and GC electrodes were essentially the same (+1.2 nA/cm^2). These *positive* values were different from the *negative* values obtained in the EtOH–water mixed solution. Thus, it may be due to the negative values of the injection noise with EtOH-containing solutions that the lower detection limit at the diamond electrode was significantly lower than that at the GC electrode in our results, compared to those obtained by Granger et al.[26]

The lower detection limits are affected by the background current, the background current noise, and the injection noise. These factors were evaluated, and two possibilities can be suggested:

(i) The overlapping with the response of AA is slight, because the background current at the diamond electrode is less than that at the GC electrode and the value of the injection noise at the diamond electrode is more negative than that at the GC electrode.

(ii) The transient current is clearly observed, because the noise of the background at the diamond electrode is less than that at the GC electrode.

Based on these considerations, it is postulated that the lower detection limit at the diamond electrode is less.

These findings suggest that the diamond electrode may be applied in the detection of other redox-active impurities and added substances in alcohol or alcohol-water solutions, such as chlorophyll, nicotinamide, riboflavin, and *dl*-α-tocopherol, etc. Actually, the detections of nicotinamide (generally contained in foods) and riboflavin (genarally contained in foods and extracted by alcohol), respectively, were investigated.

For nicotinamide, at the diamond electrode, a slight cathodic peak was observed around −1.15 V vs Ag/AgCl (not shown). However, in FIA, no current response due to nicotinamide in the injected sample was observed (not shown).

The results for caffeine and riboflavin are shown in Table 2. For caffeine, in FIA, the current responses due to caffeine in the injected sample were observed at both diamond and GC electrodes (not shown). At the diamond electrode, the *lower* detection limit was the same as that at the GC electrode. Moreover, the sensitivity at the GC electrode was 1.5 times higher than that at the diamond electrode. However, the *higher* detection limit at the diamond electrode was 3 times higher than that at the GC electrode. It may be due to the freedom from adsorption avoided by operating at low local pH at the diamond electrode rather than at the GC electrode.[41]

On the contrary, for riboflavin, the lower detection limit at the diamond electrode was 3.3 times lower than that at the GC electrode. Furthermore, at the diamond electrode, the sensitivity was 5.6 times larger than that at the GC electrode. This result at the diamond electrode suggests the superiority of the lower detection limit and the sensitivity to that at the GC electrode. The lower detection limits and the sensitivities are affected by the background current, the background current noise, and the injection noise. These two possibilities ((i) and (ii)), which are the same as the case of AA, can be suggested.

From this discussion, when using the diamond electrode as a working electrode, we have carried out FIA measurements of AA and riboflavin in an EtOH–water mixed solution containing 0.1 M $NaClO_4$ with amperometric detection, avoiding the interference from EtOH oxidation that would have been observed with a Pt electrode. Here, the diamond electrode is superior to the GC electrode thanks to its higher signal-to-

Table 2. Comparison of the Analytical Performance Characteristics for Diamond and GC Electrodes, Based on the Data of Time Dependence of the FIA Current Response When (a) Caffeine or (b) Riboflavin Is Added to the Solution at a Constant Detection Potential for Diamond or GC Electrodes in EtOH–Water Mixed Solution ($x_{EtOH} = 0.4$) Containing 0.1 M $NaClO_4$ (Sampling Interval: 2 min; Caffeine Concentration; 1 nM–1 mM; Riboflavin Concentration: 1 nM–100 μM)

(a) Caffeine*

	Diamond	GC
Higher detection limit/μM	300	100
Lower detection limit/μM	10	10
Sensitivity/nA μM^{-1}	12	18
Background current/nA cm^{-2}	5800	4300
Background noise/nA cm^{-2}	24	38
Injection noise/nA cm^{-2}	42	56

*Detection potential: +1.5 V vs Ag/AgCl.

(b) Riboflavin**

	Diamond	GC
Lower detection limit/nM	300	1000
Sensitivity/nA μM^{-1}	180	32
Background current/nA cm^{-2}	−610	−20500
Background noise/nA cm^{-2}	5.2	240
Injection noise/nA cm^{-2}	−30	−320

**Detection potential: −0.55 V vs Ag/AgCl.

noise ratio and signal-to-background ratio, which are due to its lower background current and lower injection noise. These results suggest that the application of the diamond electrode to the detection of other impurities and added substances in alcohol, such as chlorophyll and *dl*-α-tocopherol, etc., may be possible.

Conclusions

We have carried out FIA measurements of AA in an EtOH–water mixed solution containing 0.1 M $NaClO_4$ with amperometric detection at a conductive diamond electrode, avoiding the influence of EtOH oxidation that is observed for the Pt electrode. Moreover, the response of AA in the solution could be observed with a lower detection limit than that observed for a GC electrode, because the diamond electrode has a lower background current, smaller background noise, and smaller injection noise.

These results suggest that diamond electrodes may also be useful for the detection of other impurities and added substances in ethanol–water solutions, for example, alcoholic beverages. Moreover, the use of boron-doped diamond electrodes in amperometric detection results in a simplification of analytical procedure, because there is essentially no need for electrode pre-treatment or maintenance. For the future, the use of diamond electrodes for the detection of other redox-active compounds, such as chlorophyll and *dl*-α-tocopherol, etc., will be studied in alcohol and alcohol–water solutions.

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