

Research Article

Investigation of a Cu/Pd Bimetallic System Electrodeposited on Boron-Doped Diamond Films for Application in Electrocatalytic Reduction of Nitrate

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The Cu/Pd bimetallic system electrodeposited on boron-doped diamond (BDD) films for application, as electrode material in the electrochemical reduction of nitrate was studied. The electrochemical behavior of Cu, Pd, and Cu/Pd bimetallic system was evaluated by cyclic voltammetry. From these results, the formation of the Cu/Pd composite was verified. In addition, Cu with different phases and a Cu/Pd phase in the composite were obtained. Morphological analysis by scanning electron microscopy (SEM) revealed a homogeneous distribution of Cu/Pd bimetallic particles with intermediary dimensions compared to those observed in Cu or Pd electrodeposits separately. These composites were tested as electrocatalysts for nitrate reduction in Britton-Robinson buffer solution (pH 9). Electrochemical measurements showed that composites with higher Cu content displayed the best electrocatalytic activity for nitrate reduction, and the Cu/Pd phase in the bimetallic system served to improve the Cu adherence on BDD electrode.

1. Introduction

The contamination of ground and surface waters by nitrate ions has been considered a common environmental problem, especially because of the large use of nitrogen-based compounds in agriculture and industrial wastes. The necessary control and removal of nitrate ions has stimulated intensive research, because nitrate causes detrimental effects not only on human health but also on aquatic ecosystems [1, 2]. The methods which are often used for the reduction of nitrate are biological denitrification and ion exchange. However, these methods have some drawbacks such as continuous monitoring, slow kinetics, and the generation of byproduct. On the other hand, electrochemical methods have received a great deal of attention because of their advantages such as the use of clean reagents (electrons) and their low cost.

The majority of papers which deal with the electrochemical reduction of nitrate demonstrate the reaction efficiency of the single metal electrode [3–6], while some papers show the viability of the boron-doped diamond (BDD) films as an electrode material, for the electrochemical reduction of nitrate [7–10]. Particularly, BDD films are excellent electrode materials for this purpose, because of their singular physicochemical properties such as low background currents, wide potential window which analyzes the chemical species without involving water decomposition reaction, high corrosion resistance, and mechanical stability [11, 12]. In spite of the thermodynamic feasibility of the nitrate reduction, the charge transfer kinetics on BDD electrode is slow and direct reduction of nitrate has been characterized by poor sensitivity and selectivity of these electrodes. In this sense, the surface modification with a

specific electrocatalysts has been an important strategy to improve their electrocatalytic properties. In general, binary metal electrodes in the form of alloys [13, 14], codeposited films [15], or electrodes modified with foreign adatoms on their surface [16–21] have been some of the strategies used to enhance the electrode properties concerning to the electrochemical reduction of nitrate.

It is important to emphasize that BDD electrodes, due to the inert nature of their surface, are a natural substrate to make the surface modification without any major interference. Moreover, their mechanical and chemical stability permit the surface modification in the extreme conditions of preparation (e.g., high temperature) without any significant modification of the surface properties. The surface modification of BDD electrodes with Au [22–24] and Pt [25–27] nanoparticles were carried out, and interesting results were obtained. Such modifications increased the electrocatalytic activity for oxygen reduction and methanol oxidation. Recent studies also showed that the surface modification of the BDD electrodes with Cu nanoparticles obtained by simple electrochemical deposition was used to detect nitrate electrochemically using an *in situ* method [28, 29]. Besides, Cu exhibits the best electrocatalytic activity for electrochemical reduction of nitrate when compared to other materials like Ni, graphite, and Pt [30]. However, the modified BDD electrode is limited by the poor surface adherence, by the formation of toxic subproducts (nitrite and ammonia), and by the cumulative passivation effect. Up to now, bimetallic Cu/Pd electrocatalyst is considered one of the most promising materials with maximum selectivity for N_2 of 60%–70%, which is justified by its bifunctional character, in which nitrate is reduced on Cu sites into NO_2^-/NO , and subsequently reduced into N_2 on Pd sites [31, 32]. Moreover, the Cu poor adherence, previously mentioned, could also be improved when prepared in the alloy form or composite. In order to obtain such conditions, the choice of preparation method is of fundamental importance. Among the several methods used for production of alloys and composites, the electrodeposition is an interesting method due to their simplicity, their compatibility of the processing at room temperature, and their controllability of thin film properties.

To the best of our knowledge, the production of Cu/Pd bimetallic system on BDD electrodes by electrodeposition has not been studied. Nevertheless, some papers present the advantages of a Cu/Pd system electrodeposited as alloys or composite [31–35]. Vinogradov et al. succeeded in the deposition Cu/Pd alloys coating with good physicochemical properties [33]. Recently, Milhano and Pletcher produced Cu/Pd alloys coating Pt by coelectrodeposition [34]. Cu/Pd composites (without reaction between Cu and Pd) were also prepared by electrodeposition [31, 32]. Thus, this work associates the singular properties of BDD films, as electrode material, with the best conditions for the production of the Cu/Pd bimetallic system on BDD electrode. In addition, it is used as a possible composite material to be applied to the electrochemical reduction of nitrate.

2. Experimental

The BDD films were grown on silicon by hot filament-assisted vapor deposition (HFCVD) technique. The filament temperature was kept constant at 780°C. The deposition was performed for 7 h, and a gaseous mixture of 99% vol. H_2 and 1% vol. CH_4 and a total pressure of 50 Torr were used. The boron doping was obtained from H_2 forced to pass through a bubbler containing B_2O_3 dissolved in methanol. From the Mott Schottky plot, the doping level was estimated to approximately 10^{20} boron atoms· cm^{-3} [36]. The morphology of the BDD films was analyzed by scanning electronic microscopy (SEM) using a Jeol equipment JSM-5310, while that the quality was evaluated by micro-Raman scattering spectroscopy (Renishaw microscope system 2000) in backscattering configuration at room temperature employing 514 nm argon-ion laser.

All electrolytic solutions were prepared using ultrapure water from a Millipore water purifier system and analytical grade reagents were used. Prior to the experiments, the electrolytic solutions were deaerated with N_2 gas during 10 min.

Electrochemical measurements were performed using Autolab PGSTAT 302 equipment with a three-electrode cell. The BDD films were used as working electrode. The geometric area in contact with the electrolyte was 0.27 cm^2 . A platinum coil wire served as a counter electrode and Ag/AgCl electrode was chosen as the reference electrode.

Electrochemical behavior of the Cu and Pd on BDD electrodes was studied by cyclic voltammetry from solutions containing 5 mM Cu(II) + 0.5 M $HClO_4$ and 1 mM Pd(II) + 0.5 M $HClO_4$. The solutions containing Cu(II) and Pd(II) were prepared using $CuSO_4$ and $PdCl_2$ salts, respectively. With respect to the Cu/Pd composite, electrochemical studies were also realized by cyclic voltammetry using solutions containing different Cu(II) concentrations (1, 5 and 10 mM $CuSO_4$), where in these solutions, 1 mM Pd(II) and 0.5 M $HClO_4$ were maintained constant. So, (1:1), (5:1), and (10:1) Cu(II):Pd(II) ratio were used. Prior each electrochemical measurement, a mixture (3:1) HCl/HNO_3 ratio was used to clean the BDD surface. After this, BDD films maintained the same physicochemical characteristics verified in the SEM and Raman analysis.

Cu/Pd-modified BDD electrodes were produced under constant potential. Morphological analysis of the Cu/Pd composite and their composition were examined by a scanning electron microscopy (Jeol equipment JSM-5310) incorporating an energy dispersive X-ray (EDX) unit with a software for elemental analysis. In order to evaluate the composition uniformity (Cu and Pd content), multiple EDX spectra were recorded at different points over the BDD surface. Electrochemical reduction of nitrate was investigated by linear sweep voltammetry (LSV) as a function of time and deposition potential and also the Cu(II):Pd(II) ratio used for electrodeposition of the Cu/Pd composite on BDD electrode. A Britton-Robinson (BR) buffer solution (pH 9.0) without and with 0.1 M KNO_3 were used in our studies.

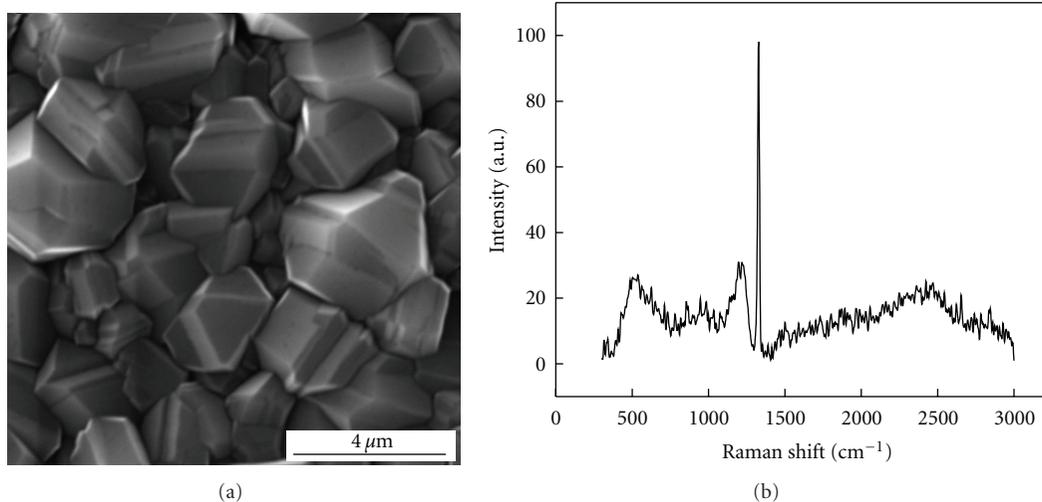


FIGURE 1: (a) SEM image and (b) Raman spectrum of the BDD film.

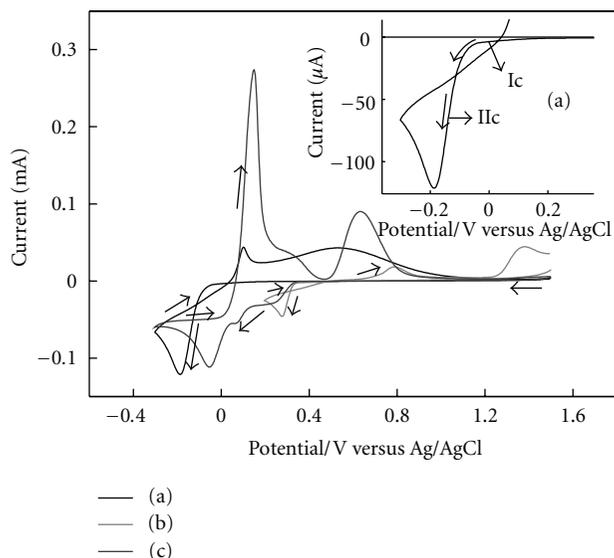


FIGURE 2: Cyclic voltammograms of the BDD electrode in solutions containing (a) 5 mM Cu(II), (b) 1 mM Pd(II), and (c) 5 mM Cu(II) + 1 mM Pd(II). All solutions containing 0.5 M HClO₄ as supporting electrolyte. Scan rate of 10 mVs⁻¹.

3. Results and Discussion

Morphological and structural characterization of BDD films was carried out prior to electrochemical experiments. Figure 1(a) shows the SEM image of the BDD film. The morphological aspect shows a film formed by symmetric and faceted grains with a uniform texture. The Raman spectra presented in Figure 1(b) confirms the quality of BDD films even after the chemical treatment with (3 : 1) (HCl:HNO₃) ratio. From the Raman spectroscopy is observed a peak at ~1320 cm⁻¹ that is characteristic of the diamond. This peak presented a shift to lower energies due to tensions caused by boron incorporation in the diamond films. In addition, the

spectrum presented two bands located at 500 cm⁻¹ and at 1230 cm⁻¹ that are associated to boron incorporation in the diamond films [37, 38].

In order to investigate the possible formation of a Cu/Pd alloy or composite on the BDD electrode, cyclic voltammetry measurements were carried out. Three different solutions were used in these experiments: one solution containing only Cu(II), the other one containing only Pd(II), and last one containing the mixture of the two metal ions. Figure 2 illustrates the cyclic voltammograms of the BDD electrode recorded at these three solutions. The curve (a) was studied in the solution containing only Cu(II), the curve (b) only Pd(II) and curve (c) a mixture of the two metal ions. The curve (a) represents the electrochemical behavior of the Cu in 5 mM Cu(II) + 0.5 M HClO₄ solution. The inset of the Figure 2(a) evidence the two regions of Cu cathodic current, labeled as (Ic) and (Iic). The first region (Ic) that begins at a more positive potential may be associated to underpotential deposition (UPD) (or intercalation) of Cu. The second region (Iic) is related to the region of bulk Cu deposition. According to Bouamrane et al., the occurrence of the UPD of Cu is related to the BDD surface condition, where it was verified to happen only in the crystalline defects, probably in the graphitic inclusions (sp² carbon sites) [39]. Besides, the UPD has been observed in other forms of carbon such as pyrolytic graphite, where it is believed to occur at sp² carbon sites which cannot be completely avoided [40]. The reverse sweep shows significant hysteresis that is consistent with the Cu deposition reaction involving nucleation as well as growth of the Cu layer. The Cu deposition continues to 0.0 V, and immediately after that, the Cu stripping is accompanied by two anodic current regions. A well-defined anodic peak at 0.05 V is associated to the maximum current of bulk Cu stripping followed by a large potential region, involving the anodic current due to the stripping of other deposited Cu phase. The overall charge balance, $Q_{\text{anodic}}/Q_{\text{cathodic}}$ ratio close to 1.0, shows that all deposited Cu was dissolved after the end of the reverse sweep. The

curve (b) represents the electrochemical behavior of the Pd in 1 mM Pd(II) + 0.5 M HClO₄ solution. The Pd deposition occurred at 0.35 V where a well-formed reduction wave was observed. The negative potential sweep was limited at 0.2 V, because from this potential, high current is observed due to hydrogen absorption into the Pd surface/lattice. Again, the reverse sweep shows substantial hysteresis with deposition continuing to 0.47 V. In this case, the $Q_{\text{anodic}}/Q_{\text{cathodic}}$ ratio was 0.47, indicating an incomplete redissolution of the Pd. The Q_{anodic} fraction indicates the residual Pd on the BDD surface, where an anodic process with a current maximum at 1.4 V is associated to the formation of the palladium oxide. The curve (c) represents the cyclic voltammogram of the Cu/Pd system obtained in 5 mM Cu(II) + 1 mM Pd(II) + 0.5 M HClO₄ solution. The deposition of the Cu/Pd system occurred in the same region of Pd deposition. The deposition process is characterized by three cathodic waves with the current maximum localized at 0.23 V, 0.07 V, and -0.05 V. This behavior may be associated with the electrodeposition of a Cu/Pd composite on BDD electrode. In this case, no alloy formation was verified (simultaneous coelectrodeposition). The more positive cathodic wave may be attributed to the reduction of Pd(II) to metallic Pd. This process was confirmed from the voltammetric study (not shown in this work). In this study, the potential sweep was reverted at -0.35 V near to the maximum current involved in the Pd deposition and revealed only the presence of the Pd deposition. As response, the resulting anodic process presented the same behavior of Pd dissolution as seen in the curve (b). The cathodic wave located at 0.07 V may be associated with the onset of the Cu deposition with different phases. One of phases may be attributed to the UPD of Cu, since it is observed at a potential region near to occurrence of the Cu UPD process, as it was discussed earlier during the electrochemical studies of Cu. On the other hand, the more negative cathodic wave at -0.05 V is confirmed to be the bulk Cu phase deposition. In spite of the more positive potential about 100 mV compared to bulk Cu deposition, the occurrence of this process is confirmed from the analysis of the reversing potential sweep, since the more positive anodic process, associated to the bulk Cu phase dissolution, begins at the same dissolution potential of the bulk Cu. Continuing the sweep to a more positive potential, an anodic current shoulder at 0.3 V is attributed to oxidation of a Cu phase followed by an anodic current wave at 0.63 V. The shifted potential to a more negative value and a high anodic charge compared to Pd dissolution process show the dissolution of a Cu/Pd phase initially electrodeposited during the negative potential sweep.

The investigation of the Cu/Pd composite on BDD electrode was carried out for three other solutions, where the Pd(II) concentration was maintained constant and Cu(II) concentration was varied. In this study, this condition was defined considering the best composition of Cu/Pd bimetallic system. As reported by Milhano and Pletcher [34], nitrate is not reduced at the Pd surface but occurs at the CuPd surface, so it is necessary to have greater Cu amount due to their high electrocatalytic activity for electrochemical reduction of nitrate. In this case, the choice of Pd for the

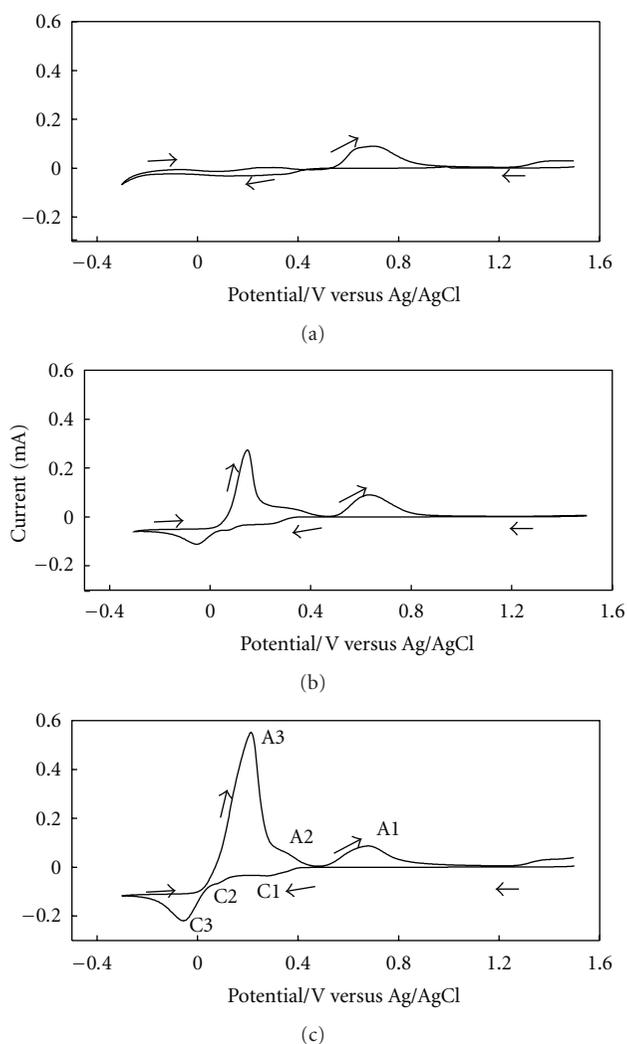


FIGURE 3: Cyclic voltammograms of BDD electrode in solutions with (a) (1 : 1), (b) (5 : 1), and (c) (10 : 1) Cu(II) : Pd(II) ratio. Scan rate of 10 mV s⁻¹.

production of a composite with Cu on BDD electrodes was made in an attempt to enhance the physical chemical properties of the Cu/Pd composite due to binding energy between Pd and Cu and also to provide active sites for obtaining nontoxic subproducts during the electrochemical reduction of nitrate.

Figure 3 presents the cyclic voltammograms of the Cu/Pd composite on BDD electrode in solutions with different Cu(II) : Pd(II) ratio. From voltammetric profiles is observed that the deposition of the Cu/Pd composite begins practically in the same potential region independently of the Cu(II) : Pd(II) ratio. In all the profiles presented, the occurrence of the two cathodic processes (C1 and C2) was observed. These processes are associated with the bulk Pd deposition and the Cu phase deposition, respectively. However, the C3 process was not evidenced for the (1 : 1) Cu(II) : Pd(II) ratio. Although an increase of the cathodic peak current intensity at -0.05 V was observed with the

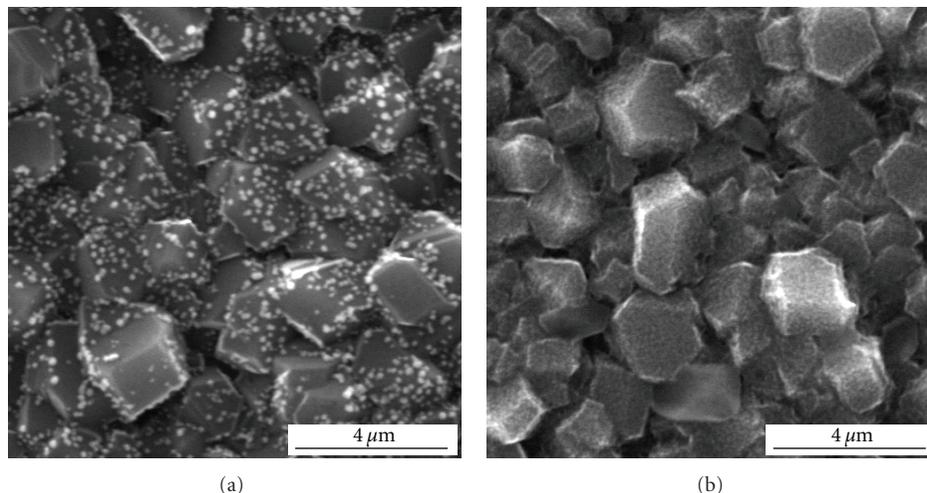


FIGURE 4: SEM images of (a) Cu and (b) Pd electrodeposited on BDD electrode. Both were deposited by 120 s, and -0.3 V and 0.2 V were applied to deposit Cu and Pd, respectively.

increase of the Cu(II):Pd(II) ratio in the solution. This result shows that increasing the Cu(II):Pd(II) ratio, thermodynamically, the simultaneous codeposition of Cu and Pd was not favored. Then, no alloying between Cu and Pd occurred. In this case, it may be only due to bulk Cu deposition with high Cu content in the Cu/Pd composite formed. In particular, hydrogen evolution reaction in the solution with (1 : 1) Cu(II) : Pd(II) ratio was observed, due to high density of catalytic Pd sites that favored the reaction. The anodic processes (A1, A2, and A3) were observed in solutions with (5 : 1) and (10 : 1) Cu(II) : Pd(II) ratio, and it may be associated to dissolution of Cu with different phases (A3 and A2 processes) and a Cu/Pd phase (A1 process) as reported earlier. The absence of A3 process in solution with (1 : 1) Cu(II) : Pd(II) ratio shows that the bulk Cu deposition did not occur. The highest anodic current intensity (A3 process) observed in solution with (10 : 1) Cu(II) : Pd(II) ratio indicates a more bulk Cu dissolution. In this process, the same current plateau commencing at 0.07 V represents a diffusion-controlled dissolution process. On the other hand, a current shoulder at -0.08 V (A2 process) and an anodic wave with current maximum at 0.63 V (A1 process) were observed in all Cu(II) : Pd(II) ratio. Independently of the Cu(II) : Pd(II) ratio, the anodic charge (~ 2.1 mC) corresponding to the A1 process presented the same value, indicating the dissolution of an identical Cu/Pd phase. The onset of the Cu/Pd phase dissolution at a more negative potential confirms the dissolution of a less noble phase compared to bulk Pd phase, as can be seen in Figure 1.

The electrochemical characterization of the Cu, Pd, and Cu/Pd composite on BDD electrode was accompanied by morphological and elemental composition analysis. Figure 4, shows the SEM images of the (a) Cu electrodeposited at -0.3 V for 120 s from a solution containing 5 mM Cu(II) + 0.5 M HClO₄ and (b) Pd electrodeposited at 0.2 V for 120 s from a 1 mM Pd(II) + 0.5 M HClO₄. The deposition

potential was defined from a region controlled by diffusion. In Figure 4(a), the SEM image reveals that Cu submicron (~ 100 nm) particles are uniformly distributed all over the BDD surface. In the case of the Pd, nanoparticles homogeneously distributed on BDD surface were produced, as shows the Figure 4(b). On the basis of these results, the morphology of the Cu/Pd composite on BDD electrodes became easier to be analyzed. The composites were produced at -0.3 V during 120 s from the solutions containing different Cu(II) : Pd(II) ratio. The SEM images are shown in Figure 5. As can be seen, all electrodeposited films were uniformly distributed on BDD electrodes. However, the size and distribution of the film particles are dependent of the solution composition. In Cu/Pd composite produced at (1 : 1) Cu(II) : Pd(II) ratio, the morphology of this particles presented intermediary dimensions compared to those of Cu and Pd electrodeposited separately. Probably, this coating refers to the deposition of a Cu/Pd phase (Figure 5(a)). This affirmation is consistent with the electrochemical results, since the bulk Cu deposition in this solution composition was not observed, as can be seen in Figure 3(a). By increasing the Cu(II) concentration, a coating of a bulk Cu phase (Figures 5(b) and 5(c)) at Cu/Pd composite was produced, since particles distribution over BDD electrode with similar dimensions to that of the Cu electrodeposit was verified. By analyzing the electrochemical behavior of the Cu/Pd composites produced at (5 : 1) and (10 : 1) Cu(II) : Pd(II) ratio, as discussed earlier in Figures 3(b) and 3(c), the morphological aspect involving particles of larger dimensions compared to Cu/Pd composite produced at (1 : 1) Cu(II) : Pd(II) ratio is associated to effect of bulk Cu deposition.

In order to obtain the Cu and Pd content in these composites, EDX analysis was carried out considering several local points ($1 \times 1 \mu\text{m}$) on BDD surface as function of the Cu(II)/Pd(II) ratio. Table 1 illustrates the elemental composition for each Cu/Pd composite. As expected, higher C content is associated with the diamond composition. On

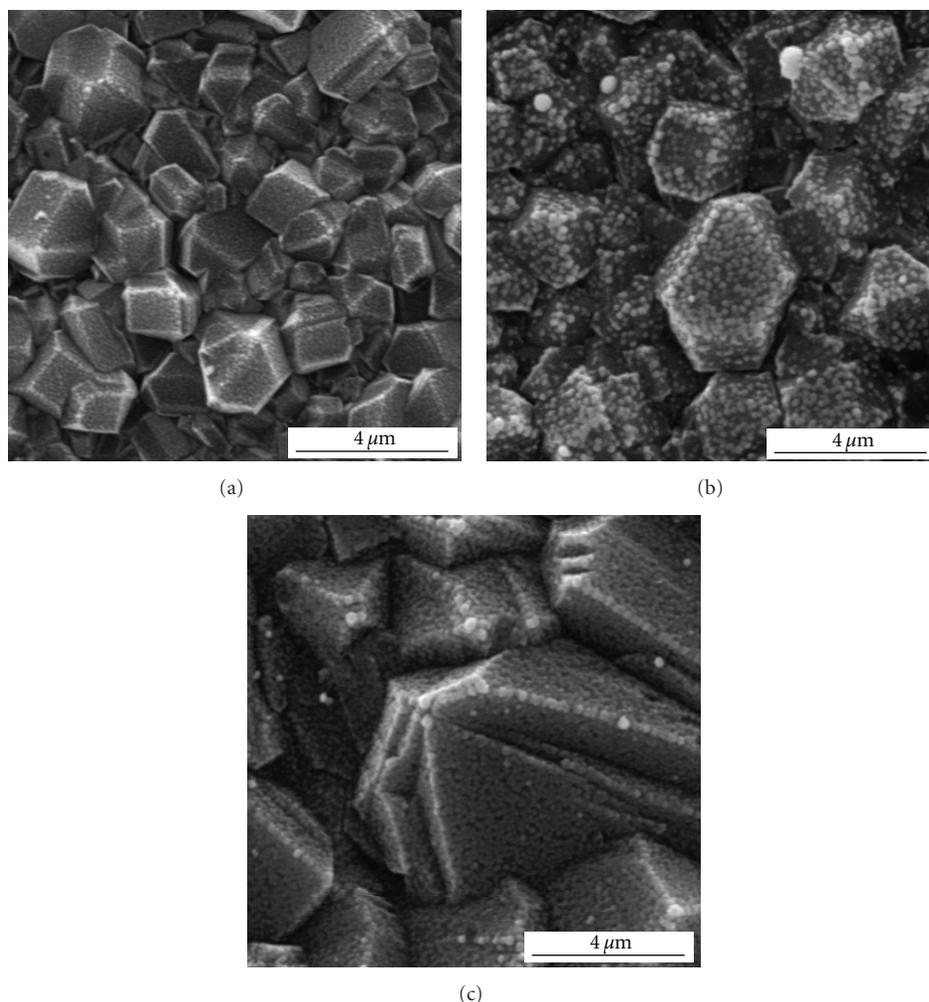


FIGURE 5: SEM images of the Cu/Pd composite electrodeposited on BDD electrode in solutions with different Cu(II) : Pd(II) ratio: (a) (1 : 1), (b) (5 : 1), and (c) 10 : 1. All were deposited applying -0.3 V by 120 s.

TABLE 1: Elemental composition (C, O, Cu, and Pd) determined by EDX analysis of the Cu/Pd composites electrodeposited on BDD electrode in solutions with different Cu(II) : Pd(II) ratio. All were deposited applying -0.3 V by 120 s.

Cu(II) : Pd(II) ratio	Composition/% at.			
	C	O	Cu	Pd
(1 : 1)	89.13	0.99	1.17	8.71
(5 : 1)	81.04	3.71	6.85	8.40
(10 : 1)	49.22	12.95	28.21	9.62

the other hand, the C content decreases, as function of the Cu(II) : Pd(II) ratio increase was verified. This result can be better visualized from the SEM image illustrated in Figure 5(c), where the BDD surface was completely covered by Cu/Pd coating. The increase of the O content in these composites may be associated to the copper oxide formation, since the O content was not found in the pure Pd electrodeposit. About 8.5% at. of Pd was found in all the Cu/Pd composites. As expected, an increase of the

atomic ratio between Cu and Pd as function of the Cu(II) concentration increase was verified.

After the electrochemical, morphological, and composition analyses, the Cu/Pd-modified BDD electrodes were used in the electrochemical reduction of nitrate. This investigation was carried out using $0.1\text{ M KNO}_3 + \text{BR}$ buffer solutions at extreme pH values (pH 1.9 and 9.0). In our initial experiments, the best condition for analyzing the nitrate response was obtained using BR buffer solution (pH 9). This condition was also achieved by other authors in their studies on Cu/Pd alloy modified by Pt and Ni electrodes [34, 35]. Figure 6(a) presents the LSV curves of the BDD electrode and Cu/Pd-modified BDD electrode in BR buffer solution pH 9. The BDD electrode shows no significant current ($3.9\text{ }\mu\text{A}$ at -1.3 V) for hydrogen evolution reaction. In contrast, the water reduction was verified to occur at more positive potentials on Cu/Pd modified BDD electrode, where a high current (0.94 mA , at -1.3 V) was involved. At -1.3 V , a current increase of 240 times confirms the high catalytic capacity of modified BDD electrode for water reduction.

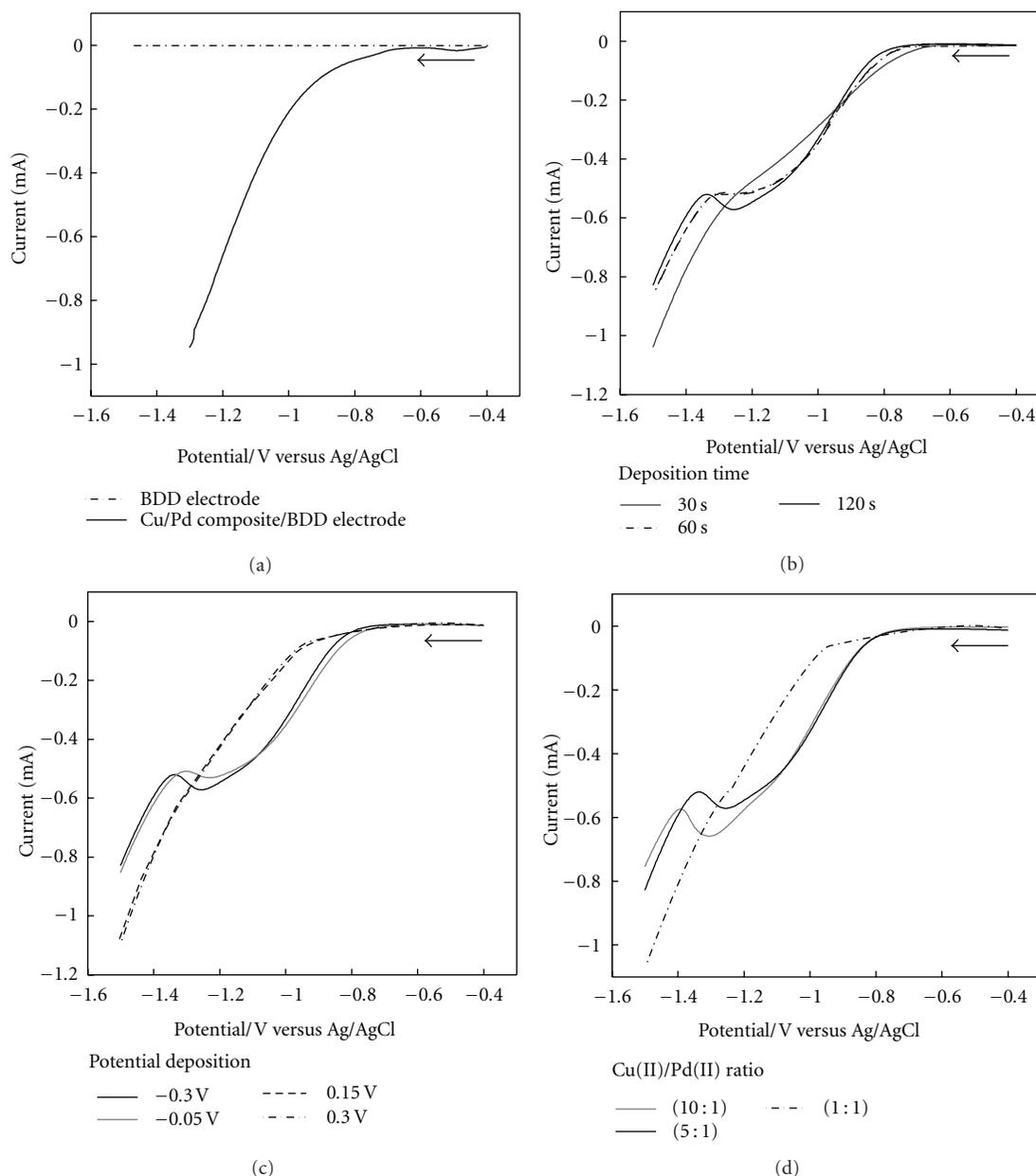


FIGURE 6: (a) LSV curves of the BDD and Cu/Pd-modified BDD electrodes in BR buffer solution (pH 9). Nitrate response of the Cu/Pd composite electrode deposited on BDD electrode at different (b) deposition time, (c) deposition potential, and (d) Cu(II):Pd(II) ratio. The nitrate response in (b) (c), and (d) was investigated in 0.1 M KNO_3 + BR buffer solution (pH 9). The Cu/Pd composite used in (a), (b), and (c) was electrodeposited using 5 mM Cu(II) + 1 mM Pd(II) + 0.5 M HClO_4 . Scan rate of 10 mV s^{-1} .

From these results, nitrate response on Cu/Pd modified BDD electrode was investigated using different electrodeposition conditions of the Cu/Pd composite such as deposition time (Figure 6(b)), deposition potential (Figure 6(c)), and Cu(II) concentration (Figure 6(d)). Such conditions were focused to obtain Cu/Pd composites with different ranges and then evaluate the nitrate reduction. The definition of scan onset from -0.4 V to -1.5 V was performed in the region where no reactions involving the Cu/Pd occur. Figure 6(b) shows the LSV curves from the Cu/Pd composite electrode deposited at different deposition time in 0.1 M KNO_3

+ BR buffer solution (pH 9). A peak current about -1.25 V is observed for the Cu/Pd composite electrode deposited by 120 s and may be attributed to nitrate reduction, which was not observed in the blank solution, as can be seen in Figure 6(a). Nitrate analysis was also carried out using Cu and Pd electrodeposits on BDD electrode for the same experimental conditions. The nitrate response on Cu-modified BDD electrode was not possible to analyze due to poor adherence of Cu, while the nitrate reduction on Pd electrodeposit was not observed due to more electrocatalytic efficiency with respect to hydrogen evolution reaction. The best nitrate

response was verified to depend on the deposition time of Cu/Pd composite, where the reduction peak current cannot be seen at short deposition time. It was also studied the nitrate response at long time of Cu/Pd composite deposition (not shown), but a negligible variation of the current peak intensity was verified. From these results, the existence of a limited time condition to produce a composite with well-defined characteristics to increase the sensitivity for the nitrate reduction is evident. A cathodic peak of nitrate reduction close to -1.25 V was also observed by Reyter et al. in their electrocatalytic tests realized in alkaline medium using Cu-Pd alloys produced on Ni electrode. In this study, maximum currents of nitrate reduction at different potentials were observed over a wide range of elemental composition [35]. Milhano and Pletcher studying Cu-Pd alloys electrodeposited on Pt microdisc electrode observed that nitrate reductions commencing close to -1.2 V in alkaline medium, but two nitrate reduction processes were noted [34].

In an attempt to enhance the efficiency of nitrate reduction, the Cu-Pd system electrodeposited at several deposition potentials, covering a wide range of elemental composition was investigated. The LSV curves are illustrated in Figure 6(c). In a potential region close to bulk Cu deposition (-0.05 V to -0.3 V), the nitrate reduction was observed. On the other hand, nitrate reduction wave at potential corresponding to the Cu/Pd phase formation ($+0.15$ V and $+0.30$ V, resp.) was not observed. Such behavior makes us believe that higher Cu content is necessary to improve the catalytic activity of nitrate reduction. In this case, the Cu/Pd phase coating may improve the adherence of Cu particles. However, electrocatalytic activity, with this coating to reduce nitrate, was not evidenced. The latter investigation involved the nitrate response using Cu/Pd-modified BDD electrode electrodeposited in solutions with different Cu(II) : Pd(II) ratio. The LSV curves are presented in Figure 6(d). From these results, it was possible to confirm all discussion previously made, where a higher cathodic current associated to nitrate reduction and commencing at the same potential was verified for the composite with higher Cu content. Besides, the peak potential shift of nitrate reduction to a more negative was verified at Cu/Pd composite electrodeposited in solution with (10 : 1) Cu(II) : Pd(II) ratio, showing a more required energy to reduce nitrate.

4. Conclusions

In this work, the electrochemical characterization in the solution containing only Cu(II) ions, Pd(II), ions and a mixture of the two metal ions performed by cyclic voltammetry was fundamental to evaluate the formation of a Cu/Pd bimetallic system on BDD electrode. From the voltammetric curves, Cu with different phases and a Cu/Pd phase were verified to be formed in Cu/Pd composite. The deposition of Cu different phases depended upon the Cu(II) : Pd(II) ratio, where the bulk Cu phase in solution with (1 : 1) Cu(II) : Pd(II) ratio was not observed. The formed Cu/Pd phase was characterized from the potential shift to more

negative values and an increase of anodic current to compare the A1 process (Cu/Pd stripping) and the bulk Pd stripping. From the morphological analysis it was possible to verify the different particles sizes deposited and also their composition. As expected, a higher Cu content was verified at the Cu/Pd composite electrodeposited in solution with highest Cu(II) concentration. On the other hand, the Cu and Pd content at Cu/Pd phase remained constant, independently of the (Cu(II) : Pd(II)) ratio used in solution. The Cu/Pd-modified BDD electrodes, tested as electrocatalysts for nitrate reduction, showed the best electrocatalytic activity for composites with higher Cu content, and formed Cu/Pd phase, was fundamental to improve the Cu adherence on BDD electrode.

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