Investigation on Electrochemically Cathodic Polarization of Boron-Doped Diamond Electrodes and Its Influence on Lead Ions Analysis

Yingying Jiang, a Dan Liu, b Zancheng Jiang, c Benjiang Mao, c Xiao Ma, a and Qibin Li b,z

a Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, Chengdu, Sichuan 611756, People’s Republic of China
b Department of Environmental Engineering, Southwest Jiaotong University, Chengdu, Sichuan 610031, People’s Republic of China
c Sichuan Belam Technology Co. Ltd., Mianyang, Sichuan 621000, People’s Republic of China

The purpose of this paper is to further understand the dependence of the electrochemical activity of a boron-doped diamond (BDD) film electrode on its surface boron doping concentration and the pretreatment applied to its surface. An electrochemically cathodic polarization (−3 V vs. SCE) with a varying polarization duration (5–50 min) was carried separately out to three types of BDDs with a boron doping level of 700, 2500, 8000 ppm in 0.5 M H2SO4 solution. Electrochemical impedance spectroscopy (EIS) and cyclic voltammogram (CV) were used to evaluate surface activity of the BDDs with and without cathodic polarizations by using 1.0 mM Fe(CN)63−/4−. Moreover, the surface activity of the polarized BDD electrodes was examined further by using anodic stripping voltammetry to detect a series of known concentrations of Pb2+. Our results indicated that the applied cathodic polarization significantly improved the surface activity of the as-received BDD, and exhibited more active effect on the surface of a higher boron doping level BDD compared to a lower boron doping level BDD, thereby improving the ability of the polarized BDDs to detect trace Pb(II) in aqueous solutions by anodic stripping voltammetry.

© The Author(s) 2014. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI:10.1149/2.106406jes] All rights reserved.

Manuscript submitted February 10, 2014; revised manuscript received May 6, 2014. Published May 15, 2014.

Boron-doped diamond (BDD) electrodes not only exhibit similar chemical-stability to that obtained in graphite and glassy carbon electrodes, but also possess a rather wide electrochemical window (＞3 V) and very low background current. Thus, it can be a promising replacement for dropping mercury electrode and classical other electrodes and very low background current. Therefore, it can be a promising replacement for dropping mercury electrode and classical other electrodes.

...
impedance tests were performed by applying a 10 mV AC signal in the 1 MHz to 0.1 Hz frequency range. The data were obtained at the open-circuit potential of the working electrode. Cyclic voltammograms were obtained at a scan rate of 50 mV/s over potential range of −0.2 V to +0.6 V. A 0.2 M KCl aqueous solution containing 1.0 mM Fe(III)/Fe(II) redox couple was used for EIS and CV tests.

Linear sweeping stripping voltammetry (LSSV) was employed to determine the concentrations of Pb(II) in 0.1 M HCl support electrolyte under the conditions in which the deposition time was set 5 min with 3 min rest period before anodic stripping voltammetry from −1.2 V to +0.6 V with a sweeping rate of 50 mV/s.

### Results

**Electrochemical impedance spectroscopy.—** In order to estimate whether the electrode surface was suitable for the redox reaction, EIS was employed to appraise the electrochemical activity of BDD electrodes by using potassium ferricyanide as a redox probe.

Figure 2a to 2c show the typical AC EIS of an as-received BDD electrode in 0.2 M KCl aqueous solution containing 1.0 mM Fe(III)/Fe(II). All of these EIS are made of a semi-circle at the high frequency part and a straight oblique line at the low frequency part, which means that the electrode reaction occurring on the electrode surface is controlled by a dynamic hybrid process containing a charge transfer and a mass transport step. The semi-circle reflects the change in surface activity of the BDD tested. In principle, the smaller the diameter of the semi-circle became, indicating that as-received BDD surface showed an obvious inhibition to the charge transfer. Furthermore, the diameter of the semi-circles decreased significantly with the cathodic polarization time, and the higher the boron doping level of the BDD was, the smaller the diameter of the semi-circle became, indicating that the cathodic polarization was more effective to a higher boron doping level BDD electrode, which is likely to be associated with the increased electron transfer rate derived from the higher surface conductivity of the BDD with high B-doping level.

In order to compare the effect of cathodic polarization quantitatively, we chose an equivalent circuit (Figure 2d) to simulate the redox process of Fe(III)/Fe(II) on the BDD surface. In the equivalent circuit, $R_{ss}$ is the sum of the solution resistance and the BDD surface resistance; $Cdl$ is electric double layer capacitor; $R_{ct}$ is charge transfer resistance; $Zd$ is diffusion resistance. Among the parameters, $R_{ct}$ is the most important parameter as its change in magnitude directly reflects the change in surface activity of the BDD tested. In principle, the smaller the $R_{ct}$ is, the higher the surface redox activity of the BDD possess. All of the data shown in Figure 2a–2c were fit-ted with the commercial softer ZsimpWin3.1 to the equivalent circuit (Figure 2d), and the fitted values of $R_{ct}$ were plotted as a function of cathodic polarization time (Figure 3). Figure 3 shows that the values of $R_{ct}$ whatever the B-dopant levels were, decreased markedly with cathodic polarization time; however, there was a distinct difference in the absolute values of $R_{ct}$ and the change rate of $R_{ct}$ with polarization duration among the three kinds of BDD samples. Evidently, BDD...
Figure 2. A complex-plane plots ((a)-(c)) for BDD electrodes after electrochemically cathodic polarization for different lengths of time in a 1.0 mM Fe(CN)$_6^{3-/4-}$/0.2 M KCl aqueous solution recorded at the open circuit potential with an ac perturbation of 10 mV, from 1 MHz to 0.1 Hz: ( ■) as received; ( ●) cathodic pretreatment for 5 min; ( ▽) cathodic pretreatment for 10 min; ( △) cathodic pretreatment for 20 min; ( ◊) cathodic pretreatment for 30 min; ( ◇) cathodic pretreatment for 50 min. (d) The equivalent circuit.

Figure 3. Influence of cathodic polarization time on $R_{ct}$.

Cyclic voltammetry.— In order to further examine the role of electrochemically cathodic polarization in improving the surface activity of BDD electrodes, a CV test was carried out on all the BDD electrodes after the EIS tests, respectively. Figure 4a–4c show the CV curves of the three kinds of boron doping level BDD electrodes in 0.2 M KCl solution containing 1.0 mM Fe(CN)$_6^{3-/4-}$. For 700 ppm BDD, a redox current peak appeared only in case of 50 min polarization (Figure 4a), and the potential difference between the oxidation and reduction peaks reached 367 mV, much larger than the value ($\sim$70 mV) that an ideal electrode surface should possess. The large peak-peak potential difference indicated that the 700 ppm BDD exhibited a very poor surface activity even if it had been cathodically polarized for 50 min. This might be a typical character of all BDD with low B-dopant.

Unlike 700 ppm BDD where no reduction peaks appeared in cases of cathodic pretreatment durations from 5 to 30 min, both 2500 and 8000 ppm BDD presented their redox peaks (Figure 4b and 4c), regardless of the polarization duration. To compare the influence of the applied cathodic pretreatments on the surface activity of BDDs, Figure 4d shows their peak-peak potential differences varying with the cathodic polarization duration. It is worth noting that, in Figure 4d, 700 ppm BDD just had one value from 50 min cathodic pretreatment due to only the pretreatment causing a reduction peak occurring. As can be seen in Figure 4d, the peak-peak potential difference of the BDDs except 700 ppm BDD decreased with cathodic polarization duration, but there were significant differences in decline rate and the absolute value of potential difference. For 2500 ppm BDD, a sharp decline in potential difference occurred at its initial polarization duration (10 min), followed by a slow decline and approach to 110 mV or so. For 8000 ppm BDD, a sharp decline occurred within 30 min initial polarization duration, followed by a mild decline and approached to 75 mV or so. A comparison of the least value of peak-peak potential difference obtained under their own optimal polarization duration, where 10 min polarization led to 110 mV for 2500 ppm BDD, and 30 min led to 75 mV for 8000 ppm BDD, was made to assess the surface activity of the polarized BDD electrodes, and the result shows that 8000 ppm BDD might be the best one among the three kinds of BDDs, being in line with the results from EIS tests.

Analyzing lead ions by linear sweeping anodic stripping voltammetry.— To evaluate the effectiveness of the cathodic pretreatments for trace metal analysis of BDD, we detected a series of known Pb$^{2+}$ concentration solutions using LSSV. Lead being chosen as an example of heavy metal ions was based on the fact that lead contamination from air, food, soil and drink water has long been a major concern. With a B-dopant level of 2500 and 8000 ppm should be suitable for electroanalysis due to their relative low electron transfer resistance.
Figure 4. Effect of cathodic polarization time on the peak-peak potential differences of the tested BDDs ((a)-(c)): cyclic voltammograms (v = 50 mV/s) for BDD electrodes in a 1.0 mM Fe(CN)₆³⁻/⁻ aqueous solution after cathodic pretreatment at −3.0 V versus SCE, for different lengths of time: (■) as-received; (●) cathodic pretreatment for 5 min; (✦) cathodic pretreatment for 10 min; (◆) cathodic pretreatment for 20 min; (◊) cathodic pretreatment for 30 min; (◆) cathodic pretreatment for 50 min. (d) The ΔEp of BDD electrodes after cathodic polarization for different lengths of time.

Figure 5. (a) LSSV response obtained for Pb²⁺ at different concentrations in a 0.1 M HCl by 8000 ppm BDD electrode after 30 minutes electrochemically cathodic polarization; (b) Linear dependence of the stripping peak current with Pb²⁺ concentration. LSSV conditions: the deposition and quiet potential were −1.2 V, the deposition time was 300 s, the quiet time was 180 s, and the sweeping rate was 50 mV/s. Ultrasonic stirring was employed during the course of deposition.

It is thus essential to evaluate environment pollution. Additionally, 700 ppm BDD electrode was not selected to be used for Pb²⁺ analysis due to its too poor surface activity.

The 2500 and 8000 ppm BDD that have been cathodically polarized for different durations, were applied to a set of known Pb²⁺ concentration solutions where C_{Pb²⁺} = 0, 20, 45, 94, 191 and 238 ppb, respectively. Figure 5 shows a typical LSSV curve of the 8000 ppm BDD that was cathodically pretreated for 30 min. From Figure 5, it can be clearly seen that the Pb²⁺ stripping peak current values increased with increasing C_{Pb²⁺} from 0 to 238 ppb, and the peak current values were plotted versus the corresponding C_{Pb²⁺}, and is also shown in the insert of Figure 5. Apparently, the curve in the insert was strictly linear within C_{Pb²⁺} from 20–238 ppb, with a regression equation I_p = 0.189C_{Pb²⁺} + 0.035, and R² was 0.99662.

The identical measurement was made three times for the same BDD electrode, and the linear coefficients of variance were found not to exceed 5%, respectively, meaning that the detections with the pretreated BDD were very reproducible.

To examine the effect of the cathodic polarization duration on the performance of the pretreated BDDs in the determination of Pb(II) in solution, like the tests applied to the 8000 ppm BDD electrode pretreated for 30 min described above, a series of Pb(II) concentration tests were also applied to the 2500 ppm BDD and the other 8000 ppm BDD electrodes that were cathodically polarized for different durations. The sensitivity and detection limit for Pb(II) of each BDD electrode pretreated were obtained by fitting a series of linear curves of the stripping peak current values versus their Pb(II) concentrations, and the resulting sensitivities and detection limits for Pb(II) were also plotted as a function of cathodic polarization durations, as shown in Figure 6.

The cathodic pretreatment time significantly influenced the Pb(II)-detecting capacity of the BDDs. With increasing pretreatment time, for both 2500 ppm BDD and 8000 ppm BDD, the sensitivity for Pb(II) increased rapidly and reached a maximum value, followed by a plateau, but significant differences are observed from Figure 6a in the maximum value of the sensitivity and in polarization time to reach the maximum value. The differences are likely due to the significant difference in boron doping level between them, because a higher boron doping concentration always generates a BDD surface with a higher density of active sites, thereby taking a longer time to hydrogenate global problem, and a rapid and accurate detection method for lead is thus essential to evaluate environment pollution.
Conclusions

Under our experimental conditions, the electrochemically cathodic polarization was demonstrated to be an effective way to increase surface activity of the as-received BDD electrodes, and the increase in the surface activity of the BDD was more effective for the BDD with a high boron doping level compared with the BDD with a low boron doing level. Moreover, the cathodically pretreated BDD electrodes exhibited a powerful ability to increase the detection sensitivity and decrease the detection limit for Pb(II). The results obtained in our tests can be helpful to select BDD type and enhance the surface activity of a BDD electrode used for electroanalysis.

Acknowledgments

This research was supported by Sichuan Belim Technology Co., Ltd. Special thanks are extended to the employees of Belam.

References

1. G. M. Swain and R. Ramesham, Anal. Chem., 65, 345 (1993).
2. P. A. Michaud, E. Mahé, W. Haenni, A. Perret, and Ch. Comninellis, Electrochem. Solid-State Lett., 3, 77 (2000).
3. C. Comninellis, Electrochim. Acta., 39, 1857 (1994).
4. V. A. Pedroza, H. B. Saffredini, L. Codognoto, S. T. Tanimoto, S. A. S. Machado, and L. A. Avaca, Anal. Lett., 38, 1115 (2005).
5. P. W. May, W. J. Ludlow, M. Hannaway, P. J. Head, J. A. Smith, and K. N. Rosser, Chem. Phys. Lett., 446, 103 (2007).
6. P. W. May, W. J. Ludlow, M. Hannaway, P. J. Head, J. A. Smith, and K. N. Rosser, Diam. Relat. Mater., 17, 105 (2008).
7. F. Pruvost and A. Deneuville, Diam. Relat. Mater., 10, 531 (2001).
8. G. R. Saltazar-Banda, L. S. Andrade, P. A. P. Nascente, P. S. Pizami, R. C. Rocha-Filho, and L. A. Avaca, Electrochim. Acta., 51, 4612 (2006).
9. S. Suzuki, C. Ama, V. Colfin, B. Marcus, D. Delabougile, and R. Bokhrouh, Electrochim. Commun., 8, 1185 (2006).
10. J. J. Wei, Ch. M. Li, X. H. Gao, L. F. Hei, and F. X. Lvun, Appl. Surf. Sci., 258, 6909 (2012).
11. W. Fortunato, A. J. Chiquito, J. C. Galerani, and J. R. Moro, J. Mater. Sci., 42, 7331 (2007).
12. H. Martin, A. Argostia, U. Landau, A. B. Anderson, and J. C. Angus, J. Electrochem. Soc., 143, 1333 (1996).
13. J. Xu, M. C. Granger, Q. Chen, J. W. Strojek, T. E. Lister, and G. M. Swain, Anal. Chem., 69, 591A (1997).
14. C. H. Goeting, F. Marken, A. Gutierrez-Sosa, R. G. Compton, and J. S. Foord, Electrochim. Acta., 39, 4617 (2000).
15. H. Girard, N. Simon, D. Baldutaud, M. Herlem, and A. Etcheberry, Diam. Relat. Mater., 16, 316 (2007).
16. H. Notsu, I. Yagi, T. Tatsuma, D. A. Tryk, and A. Fujishima, Electrochem. Solid-State Lett., 2, 522 (1999).
17. H. Notsu, I. Yagi, T. Tatsuma, D. A. Tryk, and A. Fujishima, J. Electroanal. Chem., 492, 31 (2000).
18. H. Notsu, T. Fukazawa, T. Tatsuma, D. A. Tryk, and A. Fujishima, Electrochem. Solid-State Lett., 4, H1 (2001).
19. S. Ferro and A. De Battisti, J. Electroanal. Chem., 533, 177 (2002).
20. P. B. Chaplin, D. K. Hubler, and J. Furrell, Electrochim. Acta., 89, 122 (2013).
21. M. N. Latto, G. Pastor-Moreno, and D. J. Riley, Electroanal., 16, 434 (2004).
22. H. B. Saffredini, V. A. Pedroza, L. Codognoto, S. A. S. Machado, R. C. Rocha-Filho, and L. A. Avaca, Electrochim. Acta., 49, 4021 (2004).
23. K. B. Holt, A. J. Bard, Y. Show, and G. M. Swain, J. Phys. Chem. B, 108, 15117 (2004).
24. K. P. Bachmann, W. Eberhardt, B. Kessler, H. Laide, K. Radermacher, D. U. Wiecher, and H. Wilson, Diam. Relat. Mater., 16, 531 (2001).
25. M. Tachiki, T. Fukuda, K. Sugata, H. Seo, H. Umezawa, and H. Kawarada, Jpn. J. Appl. Phys., 39, 4631 (2000).
26. J. Ristein, W. Zhang, and L. Levy, Phys. Rev. E, 78, 041602 (2008).
27. E. Brillas, M. A. Baños, M. Skoumal, P. L. Cabot, J. A. Garrido, and R. M. Rodríguez, Electrochim. Acta., 51, 105 (2006).
28. D. A. Tryk, K. Tsunozaki, T. N. Rao, and A. Fujishima, Jpn. J. Appl. Phys., 40, 4631 (2001).
29. J. J. Wei, Ch. M. Li, X. H. Gao, L. F. Hei, and F. X. Lvun, Appl. Surf. Sci., 258, 6909 (2012).
30. W. Fortunato, A. J. Chiquito, J. C. Galerani, and J. R. Moro, J. Mater. Sci., 42, 7331 (2007).
31. H. Martin, A. Argostia, U. Landau, A. B. Anderson, and J. C. Angus, J. Electrochem. Soc., 143, 1333 (1996).
32. J. Xu, M. C. Granger, Q. Chen, J. W. Strojek, T. E. Lister, and G. M. Swain, Anal. Chem., 69, 591A (1997).
33. C. H. Goeting, F. Marken, A. Gutierrez-Sosa, R. G. Compton, and J. S. Foord, Electrochim. Acta., 39, 4617 (2000).
34. H. Girard, N. Simon, D. Baldutaud, M. Herlem, and A. Etcheberry, Diam. Relat. Mater., 16, 316 (2007).
35. H. Notsu, I. Yagi, T. Tatsuma, D. A. Tryk, and A. Fujishima, Electrochem. Solid-State Lett., 2, 522 (1999).
36. H. Notsu, I. Yagi, T. Tatsuma, D. A. Tryk, and A. Fujishima, J. Electroanal. Chem., 492, 31 (2000).
37. H. Notsu, T. Fukazawa, T. Tatsuma, D. A. Tryk, and A. Fujishima, Electrochem. Solid-State Lett., 4, H1 (2001).
38. S. Ferro and A. De Battisti, J. Electroanal. Chem., 533, 177 (2002).
39. B. P. Chaplin, D. K. Hubler, and J. Furrell, Electrochim. Acta., 89, 122 (2013).
40. M. N. Latto, G. Pastor-Moreno, and D. J. Riley, Electroanal., 16, 434 (2004).
41. H. B. Saffredini, V. A. Pedroza, L. Codognoto, S. A. S. Machado, R. C. Rocha-Filho, and L. A. Avaca, Electrochim. Acta., 49, 4021 (2004).
42. K. B. Holt, A. J. Bard, Y. Show, and G. M. Swain, J. Phys. Chem. B, 108, 15117 (2004).
43. K. P. Bachmann, W. Eberhardt, B. Kessler, H. Laide, K. Radermacher, D. U. Wiecher, and H. Wilson, Diam. Relat. Mater., 16, 531 (2001).
44. M. Tachiki, T. Fukuda, K. Sugata, H. Seo, H. Umezawa, and H. Kawarada, Jpn. J. Appl. Phys., 39, 4631 (2000).
45. J. Ristein, W. Zhang, and L. Levy, Phys. Rev. E, 78, 041602 (2008).
46. E. Brillas, M. A. Baños, M. Skoumal, P. L. Cabot, J. A. Garrido, and R. M. Rodríguez, Chemosphere, 68, 199 (2007).
47. S. Y. Yagi, H. Notsu, T. Konodo, D. A. Tryk, and A. Fujishima, J. Electroanal. Chem., 473, 173 (1999).
32. F. Maier, M. Riedel, B. Mantel, J. Ristein, and L. Ley. Phys. Rev. Lett., 85, 3472 (2000).
33. D. Takeushi, H. Kato, G. S. Ri, T. Yamada, P. R. Vinod, D. Hwang, C. E. Nebel, H. Okushi, and S. Yamasaki. Appl. Phys. Lett., 86, 152103 (2005).
34. L. Ostrovskaya, V. Perevertailo, V. Ralchenko, A. Dementjev, and O. Loginova, Diamond Relat. Mater., 11, 845 (2002).
35. A. Kraft, Int. J. Electrochem. Sci., 2, 355 (2007).
36. N. Simon, H. Girard, M. Manesse, D. Ballutaud, and A. Etcheberry. Diam. Relat. Mater., 17, 1371 (2008).
37. T. N. Rao, D. A. Tryk, K. Hashimoto, and A. Fujishima, J. Electrochem. Soc., 146, 680 (1999).
38. E. Brillas and C. A. Martinez-Huitle, the Wiley Series on Electrocatalysis and Electrochemistry, p. 181-182, John Wiley & Sons, New Jersey (2011).
39. F. B. Liu, J. D. Wang, B. Liu, X. M. Li, and D. R. Chen, Diam. Relat. Mater., 16, 454 (2007).
40. R. Hoffmann, A. Kriele, H. Obloh, J. Hees, M. Wolfer, W. Smirnov, N. Yang, and C. E. Nebel, J. Appl. Phys. Lett., 97, 052103 (2010).
41. G. R. Salazar-Banda, A. E. de Carvalho, L. S. Andrade, R. C. Rocha-Filho, and L. A. Avaca, J. Appl. Electrochem., 40, 1817 (2010).
42. N. Katsuki, E. Takahashi, M. Toyoda, T. Karou, M. Iida, S. Wakita, Y. Nishiki, and T. Shimamune, J. Electrochem. Soc., 145, 2358 (1998).
43. M. C. Granger and G. M. Swain, J. Electrochem. Soc., 146, 4551 (1999).