

Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Simultaneous detection of iodine and iodide on boron doped diamond electrodes

Stéphane Fierro^a, Christos Comninellis^b, Yasuaki Einaga^{a,c,*}

^a Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama 223-8522, Japan

^b Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

^c JST, CREST, 3-14-1 Hiyoshi, Yokohama 223-8522, Japan

ARTICLE INFO

Article history:

Received 3 August 2012

Received in revised form

28 September 2012

Accepted 1 October 2012

Available online 23 October 2012

Keywords:

Iodine

Iodide

Iodate

Boron doped diamond electrodes

Electrochemical detection

ABSTRACT

Individual and simultaneous electrochemical detection of iodide and iodine has been performed via cyclic voltammetry on boron doped diamond (BDD) electrodes in a 1 M NaClO₄ (pH 8) solution, representative of typical environmental water conditions. It is feasible to compute accurate calibration curve for both compounds using cyclic voltammetry measurements by determining the peak current intensities as a function of the concentration. A lower detection limit of about 20 μM was obtained for iodide and 10 μM for iodine. Based on the comparison between the peak current intensities reported during the oxidation of KI, it is probable that iodide (I⁻) is first oxidized in a single step to yield iodine (I₂). The latter is further oxidized to obtain IO₃⁻. This technique, however, did not allow for a reasonably accurate detection of iodate (IO₃⁻) on a BDD electrode.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Iodine is an essential micronutrient, which is part of the thyroid hormones that play a role in the development of brain function and cell growth. Deficiency of iodine can lead to mental retardation, endemic goiter and could be a possible cause of stomach cancer [1,2]. In women, such deficiency can lead to overt hypothyroidism and consequent anovulation, infertility, gestational hypertension, spontaneous first-trimester abortion and stillbirth [3]. Moreover, the radioactive isotope ¹³¹I is a fission product of water nuclear reactors, which if released in natural waters, represents a biological hazard for the environment and a serious threat for global health due to its ability to heavily damage cells [4].

For all the aforementioned reasons, rapid and accurate determination of the most common iodine-containing molecules and ions found in environmental waters such as iodine (I₂), iodide (I⁻) and iodate (IO₃⁻) is critical in fields such as biological and environmental sciences. In recent years, many analytical methods have been developed to detect iodine and iodide such as chemiluminescence [5], titrimetry [6], diffuse reflectance spectroscopy [7], gas chromatography mass spectrometry [8] or ion

chromatography [9]. These techniques, however, often require complex procedures and expensive equipment, making these unsuitable for rapid and efficient detection of iodine and iodide. Electrochemical oxidation of these compounds using cyclic voltammetry, linear scan voltammetry or chronoamperometry is a potentially good alternative owing to its simplicity and high sensitivity. For these reasons, the electrochemical detection of iodide on BDD electrode was already reported [10]. For the sake of brevity, however, this study focused solely on iodide ions.

In this work, the detection of iodine and/or iodide by cyclic voltammetry on boron doped diamond (BDD) electrode is presented. The motivation behind selecting BDD arises from its outstanding properties compared to other conventional electrode materials such as a wide electrochemical potential window, low background current, excellent stability and weak adsorption of polar molecules [11,12]. These properties were shown to offer significant advantage toward the detection of As³⁺ and As⁵⁺ mixtures [13] as well as the detection of heavy metals such as selenium or cadmium [14,15]. Therefore, electrochemical oxidation through cyclic voltammetry was selected to detect iodine and/or iodide. Concentrations ranging between 0.1 and 0.5 mM were measured by cyclic voltammetry for iodine and between 0.1 and 1 mM for iodide. The oxidation mechanisms occurring at the surface of the BDD electrode are discussed. The inherent limitations of this technique, namely the accurate detection of iodate and periodate are also examined.

* Corresponding author at: Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama 223-8522, Japan.

E-mail address: einaga@chem.keio.ac.jp (Y. Einaga).

2. Experimental

2.1. Chemicals and materials

Iodine (I_2), potassium iodide (KI), potassium iodate (KIO_3) and sodium perchlorate ($NaClO_4$) were purchased from Wako. All chemicals were used without further purification.

2.2. Preparation of BDD electrodes

BDD thin films were deposited using a microwave plasma-assisted chemical vapor deposition (MPCVD) set-up (ASTeX Corp.). Acetone was used as a carbon source, and $B(OCH_3)_3$ as a source of boron. The concentration of the latter was 0.1% w/w in the source. The surface morphology and crystalline structures were characterized using scanning electron microscopy (Fig. 1). The typical size of the diamond crystals was between 3 and 5 μm . BDD films were deposited on Si (100) wafers in an MPCVD chamber at 5 kW using high-purity hydrogen as a carrier gas. The BDD film thickness was about 40 μm after a 10 h deposition period. The film quality was confirmed by Raman spectroscopy (Fig. 2). As expected, the spectrum shows only the presence of a narrow peak at 1332 cm^{-1} due to the first order scattering on the diamond (sp^3) crystal lattice. The BDD electrodes were pre-treated by ultrasonication in 2-propanol for about 10 min followed by rinsing with high-purity water to eliminate any organic impurities that may have remained within the

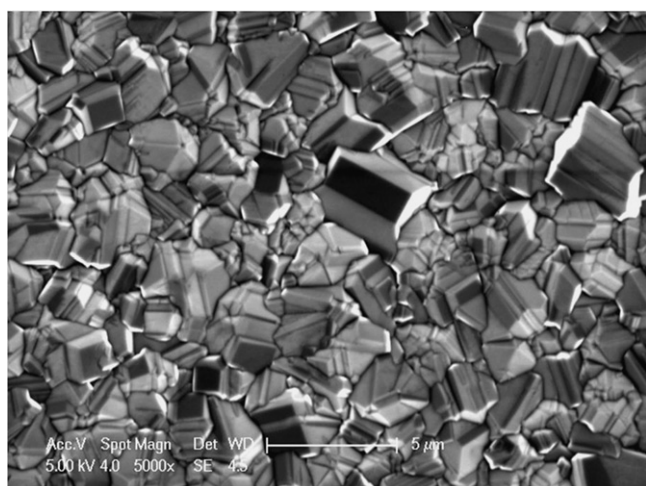


Fig. 1. Scanning electron microscopy of the boron doped diamond film with 0.1% w/w boron content.

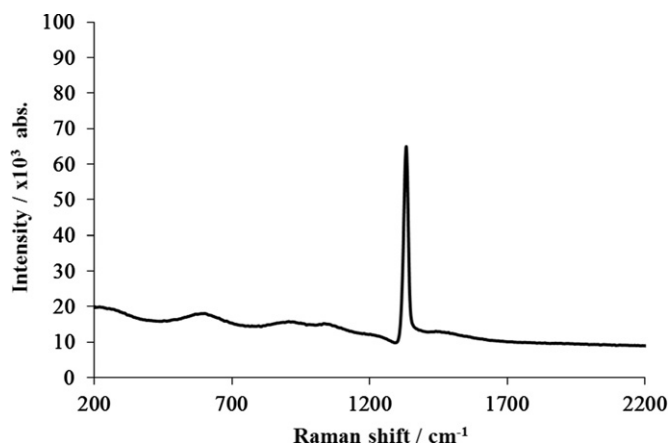


Fig. 2. Raman spectrum of boron doped diamond electrode with 0.1% w/w boron content excited by a 532 nm laser.

BDD film after deposition in the MPCVD chamber. The BDD electrodes were used without further treatment and therefore, it is believed that the diamond films used are H-terminated as observed for BDD films grown through this method [16].

2.3. Electrochemical measurements

Electrochemical measurements were carried out in a single-compartment cell using a Metrohm AUTOLAB PGSTAT30 potentiostat at room temperature ($23\text{ }^\circ\text{C}$). The reference electrode was Ag/AgCl saturated KCl, the counter electrode was a platinum wire and the working electrode was BDD. The working geometric area was 0.126 cm^2 . The electrochemical oxidation of I_2 , KI and KIO_3 was performed in 1 M $NaClO_4$. Sodium perchlorate was used as a support electrolyte because it is electrochemically inert and because the pH value of 1 M $NaClO_4$ is around 8 and is therefore reasonably representative of real samples such as environmental waters, for which the present technique is developed. Stirring was used for all experiments. All of the potentials that are quoted in this work are with respect to the Ag/AgCl saturated KCl reference electrode (0.2 V vs. SHE).

3. Results and discussion

Fig. 3A shows cyclic voltammograms of solutions containing different concentrations of KI (from 0 to 1 mM) in 1 M

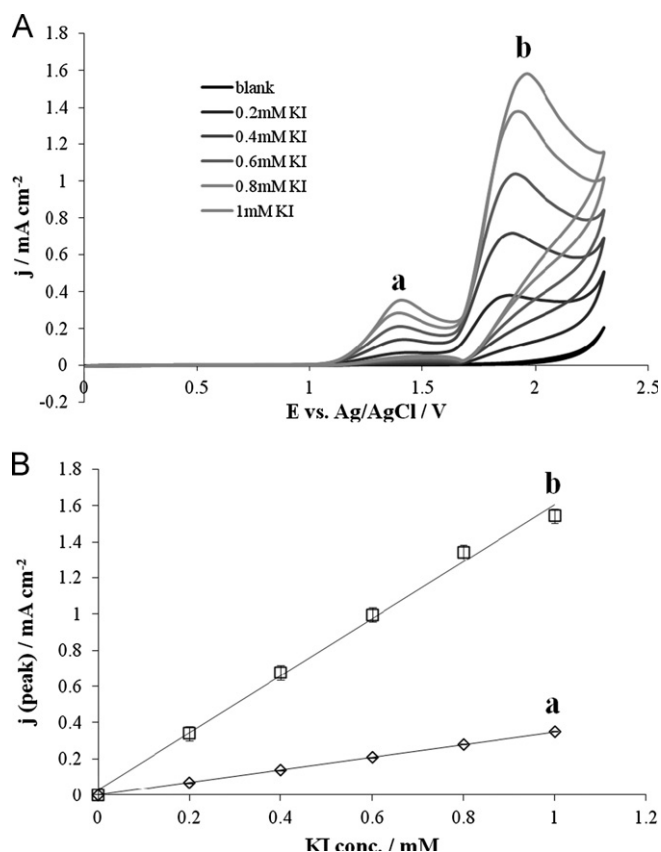


Fig. 3. (A) Cyclic voltammograms of KI solutions (different concentrations from 0 to 1 mM) recorded on BDD electrodes. Potential window between 0 V and 2.3 V vs. Ag/AgCl saturated KCl. Scan rate: 100 mV/s. (B) Calibration curves for KI detection constructed from the measurements presented in (A); the current intensities of oxidation peaks a and b were plotted as a function of KI concentration. Linear regressions characteristics: peak a—slope: 0.35 ± 0.002 , r^2 : 0.999 and peak b—slope: 1.62 ± 0.01 , r^2 : 0.995. The background current has been subtracted for all points. Support electrolyte: 1 M $NaClO_4$. $T=23\text{ }^\circ\text{C}$.

NaClO₄. This figure shows that potassium iodide starts oxidizing around 1.2 V on BDD with two well-defined oxidation peaks (i.e., between about 1.2 and 1.7 V and between about 1.7 V and 2.2 V). Furthermore, Fig. 3A shows that both peak intensities are linearly dependent on KI concentration with accuracy sufficient to build a calibration curve for the detection of KI. In fact, Fig. 3B clearly demonstrates that accurate calibration curves (peak *a*—slope: 0.35 ± 0.002 , r^2 : 0.999 and peak *b*—slope: 1.62 ± 0.01 , r^2 : 0.995) can be constructed for the detection of KI for a concentration range between 0.1 and 1 mM using cyclic voltammetry measurements. The background current corresponding to the support electrolyte has been subtracted from all points and the corresponding linear regression has been fitted to pass through the origin. Additionally, each voltammograms was performed three times in order to verify the reproducibility of the results and to estimate the uncertainties with respect to three identical sets of measurements. This procedure was performed for all calibration curves presented herein.

The lower detection limit for iodide dissolved in solution using this technique has been determined by taking three times the standard deviation observed for the results presented in Fig. 3B. Since the average standard deviation was 6 μM for peak *a* and 25 μM for peak *b*, the lower detection limits are around 20 μM and 75 μM for I[−] determination based on the current densities of peak *a* and *b*, respectively. Regarding the oxidation mechanisms involved, it is worthwhile to notice that for all concentrations of KI investigated, the current density of peak *b* is approximately five times larger than peak *a*. It is thus reasonable to suggest that the ratio of the number of electrons exchanged during both successive oxidation reactions remain the same. Consequently, the reaction corresponding to peak *a* could be the oxidation of iodide to iodine (Eq. (1)) and the reaction corresponding to peak *b* would therefore correspond to the oxidation of iodine to iodate (Eq. (2)):



These oxidation mechanisms for iodine and iodide were already reported by others in the same pH range investigated [17–21].

However, it was reported in Ref. [22], that the oxidation of iodide on BDD occurs at lower potentials (around 0.6 V vs Ag/AgCl) and is a quasi-reversible process.

In their study, the measurements were carried out using diamond films with high doping levels. Furthermore, it is known that the electrochemical behavior of highly boron doped diamond electrodes tend to resemble that of glassy carbon electrodes (higher capacitive current and narrower water stability potential window [16]) due to the presence of sp² carbon impurities in the diamond film. The difference in oxidation potential for iodide reported in Ref. [22] and in this work is therefore probably attributed to the characteristics of the diamond film used.

Fig. 4A displays similar results as in Fig. 3A but for solutions containing different concentrations of iodine (between 0.1 and 0.5 mM). The concentration range chosen for iodine was lower with respect to KI due to the low solubility of iodine. The voltammograms show the presence of a single peak corresponding to the oxidation of iodine on BDD electrodes, which is situated in the same region as the large peak observed during the oxidation of KI. Additionally, and in a similar manner as performed with KI, it is possible to determine the concentration of iodine in solution based on the correlation between the peak current density and the concentration. This calibration curve is presented in Fig. 4B and it shows that the precision of the linear regression is high (slope: 2.1 ± 0.01 , r^2 : 0.999). The detection limit

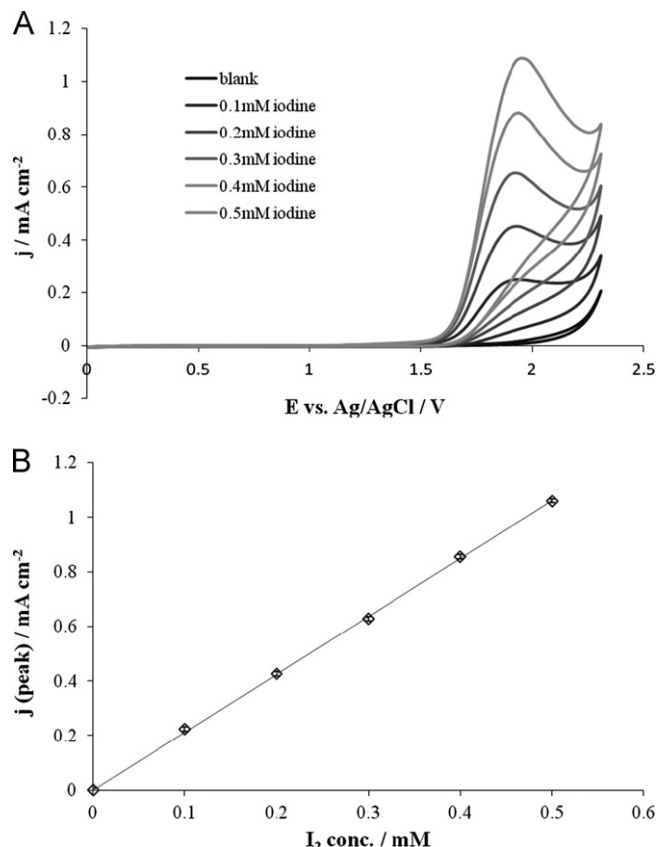


Fig. 4. (A) Cyclic voltammograms of I₂ solutions (different concentrations from 0 to 0.5 mM) recorded on BDD electrodes. Potential window between 0 V and 2.3 V vs. Ag/AgCl saturated KCl. Scan rate: 100 mV/s. (B) Calibration curve for I₂ detection constructed from the measurements presented in (A): the current intensity of the oxidation peak was plotted as a function of I₂ concentration. Linear regression characteristics—slope: 2.1 ± 0.01 , r^2 : 0.999. The background current has been subtracted for all points. Support electrolyte: 1 M NaClO₄. T=23 °C.

for iodine was again determined based on the standard deviation of the linear regression at 10 μM.

However, the difficulties to estimate the concentrations of iodine and iodide increase when both forms are mixed in the sample as it is often the case. Under these conditions, equilibrium takes place between iodine, iodide and the formation of triiodide according to the following equation (Eq. (3)):



For this reason, cyclic voltammetry measurements were carried out using solutions containing a mixture of iodine and iodide, results of which are provided in Fig. 5.

This figure indicates the presence of two oxidation peaks as for the oxidation of KI (Fig. 3A).

To attest if the concentration of I[−] can be determined from a mixture of iodide and iodine, the calibration curve constructed from peak *a* in Fig. 5 was compared with the linear regression corresponding to peak *a* in Fig. 3B. This is because oxidation peak *a* was essentially inexistent when the sample only contained iodine (Fig. 4A).

The results, displayed in Fig. 6, show that both linear regressions are almost identical and in turn demonstrate that peak *a* in Figs. 3A and 5 is related to the oxidation of iodide to iodine (Eq. (1)). Furthermore, Fig. 6 shows that it is possible to accurately determine the concentration of I[−] in the presence and absence of I₂.

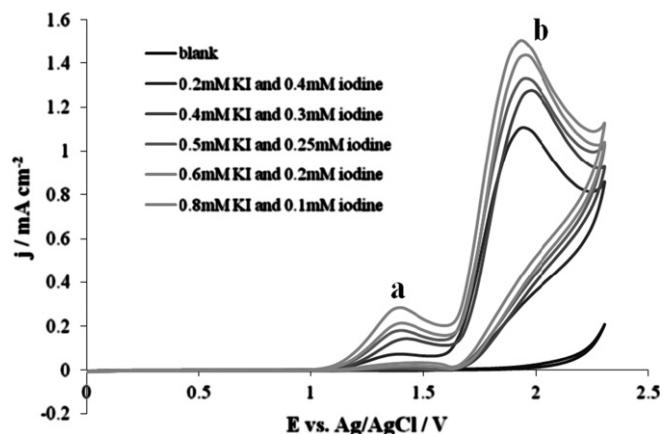


Fig. 5. Cyclic voltammograms of solutions containing different concentrations of KI and I₂ recorded on BDD electrodes. Potential window between 0 V and 2.3 V vs. Ag/AgCl saturated KCl. Scan rate: 100 mV/s. Support electrolyte: 1 M NaClO₄. T=23 °C.

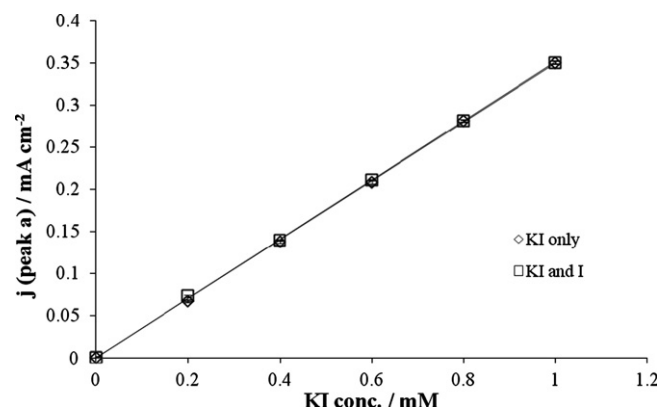


Fig. 6. Comparison between calibration curves for KI detection constructed from the measurements presented in Figs. 1 and 5: the current intensities of oxidation peak a was plotted as a function of KI concentration. Linear regression characteristics: KI only—slope: 0.35 ± 0.002 , r^2 : 0.999 and KI mixed with I₂—slope: 0.35 ± 0.002 , r^2 : 0.999. The background current has been subtracted for all points. Support electrolyte: 1 M NaClO₄. T=23 °C.

Now considering that the current intensity of peak b is higher when iodine is present in the sample with respect to only KI and that it is possible to estimate the concentration of KI in presence and absence of I₂, it could then be possible to calculate the concentration of iodine in a mixture using the results presented in Figs. 3 and 4B.

In fact, the concentration of iodine present in the mixture was calculated for each sample from the current intensity of peak a in Fig. 5 and the intensities of peak b in Figs. 3 and 4B.

Comparison between the experimental concentrations of I₂ introduced in the mixtures of I₂ and KI and the concentrations calculated from the cyclic voltammetry measurements presented in Figs. 3A and 5 were estimated. The concentration of KI in the mixture was determined from the current intensity of peak a in Fig. 5, then the current intensity of peak b in Fig. 3A was subtracted from the peak current intensity of peak b in Fig. 5. This difference in current was finally translated to the concentration of I₂ according to the calibration curve given in Fig. 4B. The results highlighted that the error between the theoretical and calculated values remains within an acceptable range for the concentration range investigated, namely around 10%.

The potential influence of other compounds present in the sample to analyze was also evaluated. Moreover, given the different redox potentials at BDD electrodes in literature [10]

a similar analysis than performed in Ref. [10] was conducted. Anions such as F⁻ and Cl⁻ should have no influence on the detection of iodine as their presence does not induce an electrochemical response in the potential region of water stability on BDD electrodes. Metals dissolved in solution such as cadmium or copper are oxidized at low potentials on BDD electrodes (before 1 V) [15] and so their presence should not be problematic either. Additionally, it has been reported that organic acids such as carboxylic acids are oxidized at potentials in the vicinity of the oxygen evolution reaction (2.2–2.3 V) [23] on BDD electrodes and should therefore pose no problem for the accurate detection of iodine and iodide. Oxidation of aromatic compounds such as phenol derivatives, however, induces the presence of well-defined peak between 1.2 and 2.3 V [24–26] and therefore could have a negative influence on the detection of iodine and iodide using the technique presented herein.

The cyclic voltammetry investigation performed in this study for iodine and iodide was repeated for iodate and the results have shown that there is essentially no difference between the blank measurement and those performed in the presence of iodate. This is an indication that iodate remains stable and is not oxidized to periodate on BDD electrode under the potential range investigated and, therefore, that the detection of iodate on BDD electrode cannot be achieved using this technique. However, it is possible to detect iodate using glassy carbon electrode as already reported in Ref. [27].

The measurements performed for the detection of iodide was repeated on glassy carbon (Fig. 7) and revealed that the detection of this compound using cyclic voltammetry measurements for a concentration ranging between 0.1 and 1 mM is also possible on this electrode material. In fact, the cyclic voltammogram of KI on glassy carbon exhibits two electrochemical couples situated approximately between 0.45 and 0.8 V and another couple situated at 1.5 V. The potential difference between the oxidation and corresponding reduction peak for the couples situated at lower potentials suggest that these processes are quasi-reversible. The presence of a third couple at 1.5 V suggests that the oxidation mechanisms of iodide on glassy carbon are different with respect to the mechanism proposed from the results obtained previously on BDD electrodes (Fig. 3). The reproducibility of the latter results, however, was far inferior with respect to BDD electrode. This is probably due to the presence of surface couples on glassy carbon electrode [28,29], which are electrochemically active and, thus, the current measured is not only related to the oxidation of iodide but also to other electrochemical reactions, which alter the

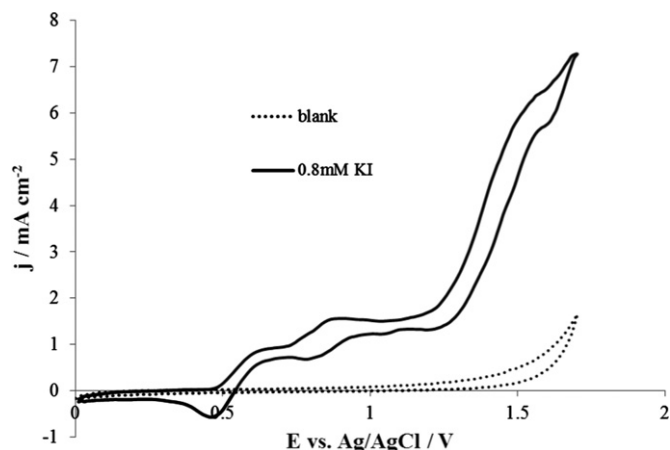


Fig. 7. Cyclic voltammogram of 0.8 mM KI solution recorded on glassy carbon electrode. Potential window between 0 V and 1.7 V vs. Ag/AgCl saturated KCl. Scan rate: 100 mV/s. Support electrolyte: 1 M NaClO₄. T=23 °C.

reproducibility of the measurements. Additionally, the peak currents corresponding to the different couples in Fig. 7 are more difficult to localize with respect to BDD electrodes owing to the higher capacitive current observed on glassy carbon electrode.

4. Conclusion

The determination of the individual and simultaneous presence of iodine and iodide in a 1 M NaClO₄ (pH 8) solution has been performed through cyclic voltammetry on BDD electrodes. The main conclusions drawn from this work are:

- Accurate calibration curves can be constructed for iodine and iodide using cyclic voltammetry measurements. The lower detection limit for the detection of these compounds on BDD electrode has been estimated around 20 μM for iodide and 10 μM for iodine.
- Based on the difference between the two peak current intensities reported during the oxidation of KI, it is suggested that I⁻ is first oxidized to iodine at approximately 1.4 V, which is in turn further oxidized to iodate (IO₃⁻) between 1.7 and 2.2 V.
- It is possible to determine the concentration of iodide in the presence and absence of iodine based on the peak current intensity corresponding to the oxidation of I⁻ to I₂. Consequently, using the peak intensities reported for the mixture and KI alone, it is possible to calculate the concentration of iodine in the mixture with reasonable accuracy.
- The method was tested on glassy carbon electrodes and the results highlighted that the oxidation mechanisms are different with respect to BDD. Additionally, the reproducibility of the results was lower with respect to BDD probably due to active surface couples on the glassy carbon electrode surface, which tend to influence the measured oxidation currents.
- Finally, it has been showed that iodate is not further oxidized to periodate on BDD electrode and under the potential range investigated. Consequently, no calibration curve for the detection of iodate could be constructed using the method presented herein.

Acknowledgments

The authors gratefully thank the Fond National Suisse pour la Recherche Scientifique (FNSRS) for their financial support. This

work was supported by the New Energy and Industrial Technology Development Organization (NEDO).

References

- [1] P. Lyn, *Altern. Med. Rev.* 13 (2008) 116.
- [2] F. Gołkowski, Z. Szybiński, J. Rachtan, A. Sokotowski, M. Buziak-Bereza, M. Trofimiuk, A. Hubalewska-Dydejczyk, E. Przybylik-Mazurek, B. Huszno, *Eur. J. Nutr.* 46 (2007) 251.
- [3] G.R. De Long, P.W. Leslie, S.H. Wang, X.-M. Jiang, M.-L. Zhang, M. Rakeman, J.-Y. Jiang, T. Ma, X.-Y. Cao, *Lancet* 350 (1997) 771.
- [4] V.V. Shakhtarin, A.F. Tsyb, V.F. Stepanenko, M.Y. Orlov, K.J. Kopecky, S. Davis, *Int. J. Epidemiol.* 32 (2003) 584.
- [5] T. Fujiwara, I.U. Mohammadzai, H. Inoue, T. Kumamaru, *Analyst* 125 (2000) 759.
- [6] G.-Z. Fang, S.-F. Gao, *Mikrochim. Acta* 136 (2001) 9.
- [7] M.P. Arena, M.D. Porter, J.S. Fritz Rapid, *Anal. Chem.* 74 (2002) 185.
- [8] H.S. Shin, Y.S. Ohshin, J.H. Kim, J.K. Ryu, *J. Chromatogr. A* 732 (1996) 327.
- [9] R.O. Rahn, *Anal. Chim. Acta* 248 (1991) 595.
- [10] J. Wu, X. Li, C. Lei, X. Wu, G. Shen, R. Yu, *J. Anal. Chem.* 60 (2005) 1062.
- [11] T. Yano, D.A. Tryk, K. Hashimoto, A. Fujishima, *J. Electrochem. Soc.* 145 (1998) 1870.
- [12] A. Fujishima, Y. Einaga, T.N. Rao, D.A. Tryk (Eds.), *Diamond Electrochemistry*, Elsevier-BKC, Tokyo, 2005.
- [13] D. Yamada, T.A. Ivandini, M. Komatsu, A. Fujishima, Y. Einaga, *J. Electroanal. Chem.* 615 (2008) 145.
- [14] S. Fierro, T. Watanabe, K. Akai, M. Yamanuki, Y. Einaga, *Int. J. Electrochem.* (2012), <http://dx.doi.org/10.1155/2012/758708>.
- [15] S. Fierro, T. Watanabe, K. Akai, M. Yamanuki, Y. Einaga, *J. Electrochem. Soc.* 158 (2011) F173.
- [16] T. Watanabe, T.K. Shimizu, Y. Tateyama, Y. Kim, M. Kawai, Y. Einaga, *Diamond Relat. Mater.* 19 (2010) 772.
- [17] L. Cantrel, R. Chaouche, J. Chopin-Dumas, *J. Chem. Eng. Data* 42 (1997) 216.
- [18] P.G. Desideri, L. Lepri, D. Heimler, in: A.J. Bard (Ed.), *Encyclopedia of Electrochemistry of the Elements*, vol. I, Marcel Dekker, New York, 1973.
- [19] M. Mastragostino, G. Casabore, S. Valcher, *J. Electroanal. Chem.* 44 (1973) 37.
- [20] V.A. Macagno, C. Giordano, *Electrochim. Acta* 14 (1969) 335.
- [21] Y.A. Yaraliev, *Russ. Chem. Rev.* 51 (1982) 566.
- [22] G. Hignett, J.D. Wadhawan, N.S. Lawrence, D.Q. Hung, C. Prado, F. Marken, R.G. Compton, *Electroanalysis* 16 (2004) 897.
- [23] D. Gandini, E. Mahé, P.-A. Michaud, W. Haenni, A. Perret, Ch. Comninellis, *J. Appl. Electrochem.* 30 (2000) 1345.
- [24] M. Panizza, I. Duo, P.-A. Michaud, G. Cerisola, Ch. Comninellis, *Electrochem. Solid-State Lett.* 3 (2000) 429.
- [25] J. Iniesta, P.-A. Michaud, M. Panizza, G. Cerisola, A. Aldaz, Ch. Comninellis, *Electrochim. Acta* 46 (2001) 3573.
- [26] M.A. Rodrigo, P.-A. Michaud, I. Duo, M. Panizza, G. Cerisola, Ch. Comninellis, *J. Electrochem. Soc.* 14 (2001) D60.
- [27] J. Jakmunee, K. Grudpan, *Anal. Chim. Acta* 438 (2001) 299.
- [28] J.C. Verhoef, E. Barendrecht, *Electrochim. Acta* 23 (1978) 433.
- [29] H.P. Boehm, M. Voll, *Carbon* 8 (1970) 227.