Contents lists available at ScienceDirect





Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Polymerisation occurrence in the anodic oxidation of phosphite on a boron-doped diamond electrode

Elisabetta Petrucci*, Daniele Montanaro, Carlo Merli

Department of Chemical Engineering Materials Environment, University of Rome "La Sapienza", Via Eudossiana 18, 00184 Roma, Italy

ARTICLE INFO

ABSTRACT

Article history: Received 26 November 2007 Received in revised form 12 February 2008 Accepted 14 February 2008 Available online 21 February 2008

Keywords: Anodic oxidation Boron-doped diamond electrode Polymerisation Phosphite Polyphosphates The electrogeneration of polymeric phosphorus compounds during the anodic oxidation of aqueous solutions of phosphites on a boron-doped diamond electrode has been studied. Although the main oxidation product is orthophosphate, the results indicate the simultaneous generation of short-chain and cyclic compounds containing two and three phosphorus atoms whose evolution has been followed by ion chromatography.

The effect on the reaction yield of several operative parameters such as current density, pH, temperature and initial phosphite concentration has been investigated.

Consistently with the data presented, a new process for the generation of polymeric phosphates is obtained.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Great attention has recently been given to the study and development of boron-doped diamond (BDD) as an electrode material in several electrochemical applications [1,2]. The interest in BDD is due to its outstanding properties such as high anodic stability and low background current, together with a wide potential window of water discharge [3–5]. The oxidation reaction has been proved to take place through different mechanisms depending on the applied potential [6]. In the range of water stability, direct electron transfer occurs, while at higher potential, the hydroxyl radical, acting as a very strong oxidising agent (E° = +2.8 V vs. NHE), is generated by water discharge.

These unique characteristics have allowed wide use of BDD electrodes as the anode in the oxidation of a broad range of organic compounds [7–11], in the treatment of a variety of industrial wastewater pollutant [12–14], water disinfection [15–17] and electrosynthesis [18–22].

A recent study, focused on treating an effluent from the manufacture of phosphorus-based flame retardants [23], confirmed the expected performance of the BDD electrode. Compared to Fenton's treatment, either chemically or electrochemically generated [24–26], BDD led to a faster and quantitative oxidation of a notable amount of hypophosphite and phosphite ions to phosphate. Apart from phosphates, oxidised forms of phosphorus include [27] polymeric compounds resulting from the condensation of two or more hydrogenophosphate units to form condensed linear polyphosphates with the generic formula $P_nO_{3n+1}^{(n+2)-}$, or metaphosphates $P_nO_{3n}^{n-}$ characterised by a cyclic structure. Major applications of these polyphosphates are in detergent and cleaner products, the food industry and water treatment as softening agents. Another class of phosphorus compounds contains a peroxide group. The most important species in this group, peroxomonophosphate and peroxodiphosphate, are mainly used as oxidising agents.

Although analytical determination of these chemicals is a critical issue [28], recent developments in the field of ion chromatography, such as electrolytic eluent generators, have allowed the detection of phosphorus compounds in aqueous media in the range of concentrations required for the present study [29].

The aim of this paper is to investigate the electrogeneration of oxidised phosphorus compounds other than phosphate when the anodic oxidation of phosphite on a boron-doped diamond electrode occurs. The influence of certain variables on the process performance is also investigated.

2. Experimental

2.1. Electrochemical equipment

All the electrolyses were performed under galvanostatic conditions using a potentiostat AMEL 2051. An undivided thermostated 100 ml cell was used stirred with a magnetic bar. A boron-doped

^{*} Corresponding author. Tel.: +39 06 44585569; fax: +39 06 44585622. *E-mail address*: elisabetta.petrucci@uniroma1.it (E. Petrucci).

^{0013-4686/\$ -} see front matter © 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2008.02.043

diamond electrode of a geometric area of 5 cm^2 constituted the anode and the counter electrode was a platinum wire. Unless otherwise specified, all the experiments were conducted on solutions containing 16 mM of sodium phosphite, $T = 20 \,^{\circ}\text{C}$ and $j = 100 \,\text{Am}^{-2}$. Since the initial pH of this solution was 8.3, the addition of 1N sulphuric acid was needed for tests carried out at pH 2 and pH 7, while a pH value of 12 was achieved by the addition of 1N sodium hydroxide.

Experiments were replicated at least three times.

2.2. Analysis

pH was measured with a Crison GLP 421 pH meter. The concentration of total phosphorus was determined by a UV-vis spectrophotometer according to standard methods [30]. The ionic species concentration was determined by a Dionex 120 ionic chromatograph equipped with an IONPAC AS16 anionic column and an ASRS ULTRA II suppressor. This system was updated with an RFC 30 eluent generator that provided for electrolytic production of high-purity hydroxide eluent with gradient capabilities.

The method of analysis developed for this work utilized an eluent gradient from 15 mM at 0 min to 65 mM at 30 min, a flow rate of 1.5 ml min⁻¹ and an injection volume of 25 μ l.

The inorganic ionic species were identified through comparison to commercial and prepared standards. The phosphate, phosphite and hypophosphite standards were prepared from the corresponding sodium salts (Na₃PO₄, Na₂HPO₂ and NaH₂PO₂) supplied by Merck. Sodium pyrophosphate (Na₄P₂O₇·10H₂O), sodium trimetaphosphate (Na₃P₃O₉), sodium tripolyphosphate (Na₅P₃O₁₀) were supplied by Sigma–Aldrich.

Sodium tetrametaphosphate (Na₄P₄O₁₂) was prepared by low temperature hydration of phosphorus pentoxide [31] while peroxodiphosphate was electrochemically synthesized starting from aqueous solutions of phosphate as described by Cañizares et al. [21]. Hypophosphate was obtained through oxidation of red phosphorus with hydrogen peroxide under alkaline conditions [32] and tetrapolyphosphate from hydrolysis of tetrametaphosphate [33]. Since the reaction yield in the synthesis of tetrametaphosphate, peroxodiphosphate and hypophosphate was not exactly calculated, only semiquantitative analyses of these compounds were conducted. The identification of all the examined phosphorus compounds was confirmed by means of electrospray mass spectrometry.

3. Results and discussion

3.1. Electrolyses

During the study of the anodic oxidation of phosphite using a BDD electrode, in a few of the experiments, when sulphuric acid instead of hydrochloric acid was used as the supporting electrolyte, unexpected behaviour was observed. At the end of the oxidation treatment, although spectrophotometric determinations had verified the total phosphorus content, the concentration of orthophosphate, determined by means of ionic chromatography, was lower than that stoichiometrically expected. This result provides evidence for the generation of soluble oxidised phosphorus compounds other than phosphate that are not detectable with the used chromatographic technique. After updating the DX120 as described in Section 2.2, it was possible to verify that, although phosphate represents the main product, significant amounts of polymeric phosphorus compounds were also observed. The order of elution of phosphorus compounds obtained with the developed chromatographic method is shown in Fig. 1, where IC signal intensity is expressed as a function of retention time. In particular, all



Fig. 1. Elution order of compounds (–) from electrolysis of 16 mM phosphite ($j = 100 \text{ Am}^{-2}$, V = 100 ml, pH 2, T = 20 °C, time of electrolysis = 2 h) including spiked compounds (–––). Peak identification: (1) hypophosphite, (2) phosphite, (3) sulphate, (4) phosphate, (5) unknown peak, (6) trimetaphosphate, (7) hypophosphate, (8) pyrophosphate, (9) peroxodiphosphate, (10) unknown peak, (11) tripolyphosphate, (12) tetrametaphosphate, (13) tetrapolyphosphate.

the peaks deriving from a 2-h electrolysis of 16 mM phosphite ($j = 100 \text{ Am}^{-2}$, pH 2) are shown as solid lines, while the spiked compounds hypophosphite, hypophosphate, tetrametaphosphate, and tetrapolyphosphate are shown as dotted lines. The elution order, except for trimetaphosphate, is consistent with the general rule according to which the retention time directly depends on charge and molar mass. The electrogeneration of polymeric compounds was unequivocally confirmed by means of electrospray mass spectrometry where traces of P compounds with n > 4 were also found.

At the end of the same electrolysis, when the overall disappearance of phosphite was observed, the concentration of phosphate was 12.8 mM, trimetaphosphate 2.3 mM and pyrophosphate 0.9 mM.

To better understand how the operating conditions affect the electrogeneration of polymeric compounds, a study focusing on peroxodiphosphate ($P_2O_8^{4-}$), pyrophosphate ($P_2O_7^{4-}$) and trimetaphosphate ($P_3O_9^{3-}$) was conducted. The relevance of these compounds lies both in their significant concentration and in their being representative of three different classes of phosphorus compounds: diperoxide, linear and cyclic polyphosphates.

The influence of current density on the production of polymeric compounds was studied in the range from 50 to $200 \,\text{Am}^{-2}$ in galvanostatic electrolyses of 16 mM phosphite solutions at pH 2. The data reported in Fig. 2, where the temporal evolutions of all the main products are presented, indicate that an increase in the current density results in an enhanced production of phosphate. On the contrary, trimetaphosphate was found to be notably sensitive to the current applied, doubling its maximum concentration when current density was halved. This is despite an initial trend, in which trimetaphosphate was apparently independent of the current density especially when j = 50and 100 A m⁻². In general, after a rapid increase, the curves tend toward a quasi-steady state concentration. A similar trend is also observed for peroxodiphosphate, even though its concentration reaches comparable values at higher current density and significantly rises only at 50 A m⁻². A considerably different behaviour is seen for pyrophosphate, whose concentration is nearly unaffected by current and grows continuously, although at a very low rate.



Fig. 2. Effect of current density on temporal evolution of (a) phosphate, (b) trimetaphosphate, (c) peroxodiphosphate and (d) pyrophosphate. $j = 50 \text{ Am}^{-2} (\Box), j = 100 \text{ Am}^{-2} (\bigcirc), j = 200 \text{ Am}^{-2} (\bigtriangleup), [P]_i = 16 \text{ mM}, V = 100 \text{ m}, P = 20 \text{ c}.$

Given that an increasing current density is expected to enhance the generation of hydroxyl radicals, the higher production of phosphates observed in the tests suggests that their formation occurs through a reaction mediated by hydroxyl radicals. Moreover the use of different anode materials (i.e. graphite), known to be unable to produce hydroxyl radicals, led to very little phosphate production. This result likewise inidicates that the oxidation process of phosphite using a BDD anode has to be attributed to hydroxyl radicals as follows:

$$HPO_3^{2-} \stackrel{\bullet OH}{\longrightarrow} PO_3^{2-} \tag{1}$$

$$^{\bullet}\mathrm{PO}_{3}^{2-} \xrightarrow{^{\bullet}\mathrm{OH}} \mathrm{PO}_{4}^{3-}$$

$$\tag{2}$$

On the other hand, the electro-generation of the other oxidised compounds, being favoured by a lower current density, suggests the occurrence of a different mechanism involving hydroxyl radicals as well, in competition with the oxidation to phosphate. According to these results, the production of polymeric compounds seems to be favoured when the ratio between the hydroxyl radicals and the phosphite concentration is lower. To support this hypothesis a series of tests were thus performed at different initial concentrations of phosphite in electrolyses conducted under the same conditions of current density.

The temporal evolution of the phosphorus compounds generated during electrolyses of solutions at initial phosphorus contents ranging from 9.6 to 29 mM is illustrated in Fig. 3. As can be seen, the amount of pyrophosphate, trimetaphosphate and peroxodiphosphate increases with the initial concentration of phosphite. Different formation yields (calculated as the ratio of the final concentration of each compound to initial phosphite) were also observed. In particular, the production yield varied from 3% to 29% for trimetaphosphate, from 3% to 15% for peroxodiphosphate and from 1% to 8.5% for pyrophosphate at the expense of phosphate, whose production yield dropped from 100% to 58%. This result can be explained considering that, under the same conditions of current density, i.e. in the presence of the same amount of hydroxyl radicals, and increasing the concentration of phosphite, that means reducing the ratio between hydroxyl radicals and phosphite, a reaction pathway different from the hydroxylation to phosphate (Eq. (2)) seems to be favoured.

To study the influence of pH on the concentration of phosphorus compounds, a series of tests were then performed on 16 mM phosphite solution at 100 A m⁻². Data referring to runs conducted at pH 2, 7 and 12 are reported in Fig. 4. As shown, by increasing the working pH, not only a higher initial rate of phosphate production was observed but also a different final concentration was found. The difference in the amount of final phosphate is attributed to the electrogeneration of compounds other than phosphate that reach a maximum under acidic conditions. In particular, passing from pH 2 to pH 7, a significant effect on peroxodiphosphate and pyrophosphate production was observed while trimetaphosphate, in the same range, shows high and comparable concentrations. Working at pH 12, apart from phosphate, very scarce concentrations of polymeric phosphates are produced. Data not reported here indicate that the phosphite removal rate is pH independent, suggesting that the generation mechanism of all the products occurs through a first common step that transforms phosphite into an intermediate species via a reaction not influenced by pH. Nevertheless, pH appears to be crucial when the reaction evolves into the final compounds.

A beneficial effect on the rate of the reactions, which is expected with increasing temperature, is confirmed by the evolution of phosphite in a range varying from 10 to 40 °C (data not shown for clarity). On the other hand, an almost constant production is found for phosphates under the same conditions, as shown in Fig. 5. This implies that temperature positively affects a reaction pathway different from that leading to phosphate (Eq. (2)), favouring in particular the cyclization into trimetaphosphate. As illustrated in the same figure,



Fig. 3. Effect of initial phosphite concentration on (a) phosphate, (b) trimetaphosphate, (c) peroxodiphosphate and (d) pyrophosphate. [P]_i = 9.7 mM (□), [P]_i = 16 mM (○), [P]_i = 29 mM (△). V = 100 ml, j = 100 A m⁻², pH 2, T = 20 °C.



Fig. 4. Effect of pH on temporal evolution of (a) phosphate, (b) trimetaphosphate, (c) peroxodiphosphate and (d) pyrophosphate. pH 2 (\Box), pH 7 (\bigcirc), pH 12 (\triangle). [P]_i = 16 mM, V = 100 ml, j = 100 A m⁻², T = 20 °C.



Fig. 5. Effect of temperature on temporal evolution of (a) phosphate, (b) trimetaphosphate, (c) peroxodiphosphate and (d) pyrophosphate. $T = 10 \degree C(\Box)$, $T = 20 \degree C(\bigcirc)$, $T = 40 \degree C(\bigtriangleup)$, (\triangle) . [P]_i = 16 mM, V = 100 ml, j = 100 A m⁻², pH 2.

pyrophosphate appears to be insensitive to temperature even if the low concentration produced does not allow a good evaluation of the effect. Similar behaviour is presented by peroxodiphosphate, which shows different concentrations, after the initial almost constant trend. This is due to the concomitant occurrence of thermal decomposition, most likely to phosphate.

3.2. Discussion

The data presented above show that a variety of oxidised phosphorus polymeric compounds besides phosphates can be produced in acidic or circum-neutral media on a BDD electrode at a current density of below $200 \,\mathrm{Am^{-2}}$ also at room temperature. Although further investigation is needed to ascertain the oxidation and polymerisation mechanisms and also the actual radical species involved, a few remarks can be made in accordance with the experimental evidence.

Since phosphite has a readily abstractable proton, the oxidation process can cause cleavage of the P-H bond, leading to the formation of a phosphorus-centred radical (Eq. (1)), which is subsequently oxidized to the main final product, phosphate (Eq. (2)). Although possible, the dimerization via phosphite radical to form hypophosphate was not evidenced. To explain the formation of the phosphorus polymeric compounds, characterised by a sequence of oxygen and phosphorus intermolecular bonds, a further oxidation reaction has to be assumed involving the activation of an oxygen atom. This likely occurs through the formation of an oxygencentred radical, which seems possible at the conditions used here only starting from phosphite ions. In fact, unlike the findings of previous work [21], the electro-generation of polymeric compounds from phosphate has to be excluded since, preliminary experimental tests, proved the total unreactivity of phosphate under the milder operative conditions ([P]_i = 16 mM, pH 2, j = 100 A m⁻², undivided cell) adopted for this work.

4. Conclusions

The anodic oxidation of phosphite solutions on a borondoped diamond electrode results in the electrogeneration of not only phosphate but also peroxodiphosphate and other polymeric compounds, mainly pyrophosphate and trimetaphosphate, whose production depends on the operative conditions. Low current density and high concentration have been proven to be beneficial while increasing pH strongly affects the formation of these products. Increasing the temperature tends to suppress peroxodiphosphate, does not affect pyrophosphate, and notably enhances only trimetaphosphate production.

For a better understanding of the mechanism involved, further studies are in progress also considering hypophosphite as the oxidizable species.

Acknowledgements

The authors are grateful to Prof. C. Furlani for his helpful discussion on reaction mechanisms and Dr. L. Salvini for analyses by electrospray mass spectrometry.

References

- [1] M. Panizza, G. Cerisola, Electrochim. Acta 51 (2005) 191.
- [2] A. Kraft, Int. J. Electrochem. Sci. 2 (2007) 355.
- [3] J. Xu, M.C. Granger, O. Chen, J.W. Strojek, T.E. Lister, G.M. Swain, Anal. Chem. 69 (1997) 591.
- [4] G. Foti, D. Gandini, C. Comninellis, A. Perret, W. Haenni, Electrochem. Solid-State Lett. 2 (1999) 228.
- [5] I. Duo, P.A. Michaud, W. Haenni, A. Perret, C. Comninellis, Electrochem. Solid-State Lett. 3 (2000) 325.
- [6] J. Iniesta, P.A. Michaud, M. Panizza, G. Cerisola, A. Aldaz, C. Comninellis, Electrochim. Acta 46 (2001) 3573.
- [7] D. Gandini, E. Mahé, P.A. Michaud, W. Haenni, A. Perret, C. Comninellis, J. Appl. Electrochem. 30 (2000) 1345.

- [8] G. Lissens, J. Pieters, M. Verhaege, L. Pinoy, W. Verstraete, Electrochim. Acta 48 (2003) 1655.
- [9] M. Mitadera, N. Spataru, A. Fujishima, J. Appl. Electrochem. 34 (2004) 249.
- [10] A. Polcaro, A. Vacca, M. Mascia, S. Palmas, Electrochim. Acta 50 (2005) 1841.
- [11] E. Brillas, M.A. Baños, M. Skoumal, P.L. Cabot, J.A. Garrido, R.M. Rodríguez, Chemosphere 68 (2007) 199.
- [12] A. Kraft, M. Stadelmann, M. Blaschke, J. Hazard. Mater. B 103 (2003) 247.
- [13] K. Van Hege, M. Verhaege, W. Verstraete, Water Res. 38 (2004) 1550.
- [14] P. Cañizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Sáez, Water Res. 39 (2005) 2687.
- [15] P.A. Michaud, M. Panizza, L. Ouattara, T. Diaco, G. Foti, C. Comninellis, J. Appl. Electrochem. 33 (2003) 151.
- [16] M.E.H. Bergmann, J. Rollin, Catal. Today 124 (2007) 198.
- [17] S. Palmas, A. Polcaro, A. Vacca, M. Mascia, F. Ferrara, J. Appl. Electrochem. 37 (2007) 1357.
- [18] A. El Ghazali, S. Belcadi, J.J. Rameau, F. Dalard, J. Appl. Electrochem. 28 (1998) 725
- [19] J. Iniesta, P.A. Michaud, M. Panizza, C. Comninellis, Electrochem. Commun. 3 (2001) 346.
- [20] K. Serrano, P.A. Michaud, C. Comninellis, A. Savall, Electrochim. Acta 48 (2002) 431.

- [21] P. Cañizares, F. Larrondo, J. Lobato, M.A. Rodrigo, C. Sáez, J. Electrochem. Soc. 152 (2005) D191.
- [22] P. Cañizares, M. Arcís, C. Sáez, M.A. Rodrigo, Electrochem. Commun. 9 (2007) 2286. [23]
- D. Montanaro, E. Petrucci, C. Merli, J. Appl. Electrochem. (2008), doi:10.1007/s10800-008-9501-y.
- [24] L. Di Palma, C. Merli, E. Petrucci, Ann. Chim. Rome 91 (2001) 145.
- [25] L. Di Palma, C. Merli, E. Petrucci, Ann. Chim. Rome 93 (2003) 935.
 [26] A. Da Pozzo, P. Ferrantelli, C. Merli, E. Petrucci, J. Appl. Electrochem. 35 (2005) 391
- [27] Ullmann's Encyclopedia of Industrial Chemistry, 7th ed., John Wiley & Sons, New York, 2007.
- [28] V. Ruiz-Calero, M.T. Galceran, Talanta 66 (2005) 376.
- [29] Dionex, IonPac AG16 Manual, Dionex Corporation, Sunnyvale, 2005.
 [30] APHA, AWWA, WPCF, Standard methods for the examination of water and wastewater, 17th ed., Baltimore, MA, 1989.
- R.N. Bell, L.F. Audrieth, O.F. Hill, Ind. Eng. Chem. 44 (1952) 568. [31]
- [32] N. Yoza, S. Ohashi, Bull. Chem. Soc. Jpn. 38 (1965) 1408.
- [33] J. Crowther, A.E.R. Westman, Can. J. Chem. 34 (1956) 969.