

Phosphate Oxidation on Boron Doped Diamond Electrode

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Abstract: The electrochemical study shows that phosphate ions oxidation on BDD (Boron Doped Diamond) occurs before oxygen evolution in aqueous mild. The reaction rate is enhanced in a basic solution.

With voltametric studies it is shown that oxidation current is linearly dependent on phosphate ions concentration and potential scan rate. The electro-chemical mechanism is very complex and involves several steps with adsorbed species and radicals.

The electrolysis at fixed potential leads to peroxodiphosphate species formation in solution.

The complexity of electrochemical mechanism is confirmed by EIS study. EIS measurements demonstrate also that BDD electrode-electrolyte behavior is compatible to p-type semiconductor with 1.49 V as plate band potential.

Keywords: BDD - phosphate oxidation – peroxodiphosphate - voltametric study - electrolysis – EIS measurements.

1. INTRODUCTION

The knowledge of the electro-chemical behaviour of the phosphate ions oxidation on BDD is of a great interest to elaborate new applications in the residuary water treatment domain [1-5]. Several techniques using BDD have been elaborated for radioactive garbage detection [5], nitrates reduction [6] and water decontamination [7].

Peroxophosphates in general and peroxodiphosphates in particular are actually of a great interest in various industrial domains. This is attested by the many patents recorded in the last decade. Indeed, besides their use in analytical chemistry and in organic synthesis [8], the peroxodiphosphates are also used in cosmetic [9-13], in agriculture [14], in biology [15-16], in pharmaceutical industry [17] and in the environment protection sciences [18]. Their interest also spreads to heavy metals recuperation and metallurgy where they are used as corrosion inhibitors and on surfaces of metallic prostheses in biological environment [19]. Polymers elaboration and textile manufacturing are also sectors in where peroxodiphosphates are of a current use.

Boron-doped diamond (BDD) electrodes have been largely investigated during the last decades because of their excellent electrochemical properties, such as wide potential window, low back-

ground current, ultra-stability and biocompatibility [20]. The applications of BDD electrodes in electrochemical analysis, electrochemical synthesis, wastewater treatment and supporting catalyst have attracted many interests. Comparing to classical electrodes, BDD electrode is one of the best electrodes for oxidation with important faradic yield, without promoters' addition as the case for conventional electrodes [21].

Up to now, there are few studies reported in the literature on the phosphate ions oxidation on BDD support [22]. However, numerous works are reported about their oxidation on different electrode materials like platinum [23- 26]. The first electro-synthesis of the peroxodiphosphate product has been realized in 1910 [27]. The peroxodiphosphate production on an industrial scale remained restricted because of the weak electro-chemical yield. This is due to the fact that at anodic potential, on platinum electrode, a competitive reaction leading to oxygen formation occurs simultaneously with oxidation process [28].

The resulting change at anode surface state modifies the reaction kinetics and consequently the peroxodiphosphate formation yield. On the other hand, the phosphate ions oxidation on BDD electrode is enhanced toward oxygen evolution.

In this work we are interested to anodic phosphate ions oxidation on the BDD in aqueous solution within the following objectives:

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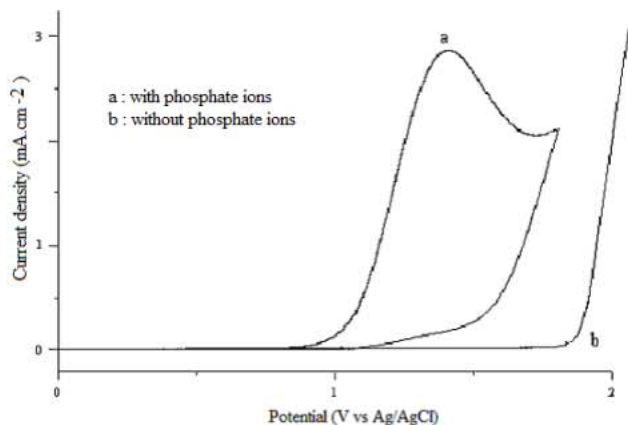


Figure 1. $i(E)$ curves of a BDD electrode : $[\text{PO}_4^{3-}] = 0.1 \text{ M}$; $\text{pH} = 12$; $v = 50 \text{ mV/s}$.

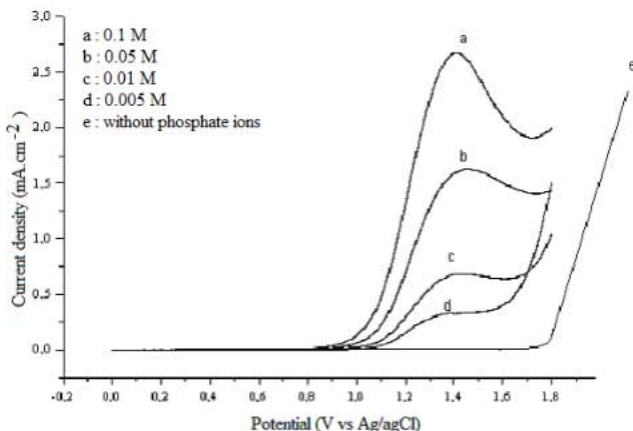


Figure 2. $i(E)$ curves of BDD electrode at different concentrations of phosphate ions; $\text{pH} = 12$; $v = 50 \text{ mV/s}$.

- To elucidate the electrochemical oxidation mechanism of phosphate ions.

- To give worth to the phosphate salt by elaborating strong oxidant as peroxodiphosphate product.

2. EXPERIMENTAL SECTION

The voltametric measurement, EIS study and electrolysis were carried out with potentiostat type PGZ 100 (Voltalab 40 Radiometer Analytical) monitored by computer with Voltmaster 4 software. Electrochemical impedance spectroscopy (EIS) measurements were performed with superimposed sinusoidal signal excitation amplitude of 10 mV. The impedance spectra were recorded in the frequency range 0.1 Hz-100 kHz.

The cell used for the electro-chemical measurements is of 200 ml capacity. The working electrode is BDD type (supplied by CSEM) with medium doping level of 500 ppm and 0.28 cm² area. All potential values are reported to Ag/AgCl reference electrode. Phosphate ions are introduced in solution as Na₂HPO₄. All the used chemical products are of analytical quality.

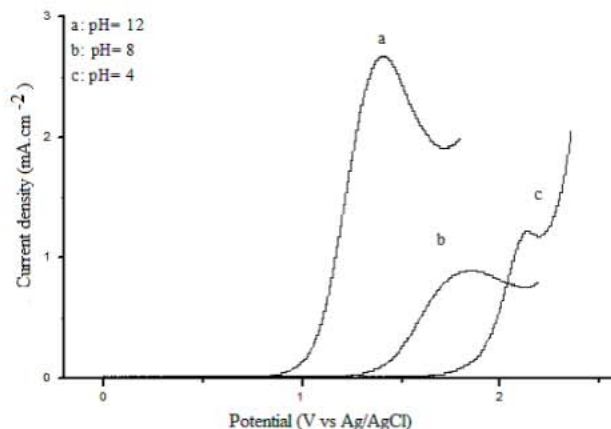


Figure 3. $i(E)$ curves of a BDD electrode at different pH : $[\text{PO}_4^{3-}] = 0.1 \text{ M}$ $v = 50 \text{ mV/s}$.

Electrolysis experiments are realized in separated compartments (anodic and cathodic). All experiments are performed at room temperature.

3. RESULTS AND DISCUSSION

3.1. Results

3.1.1. Voltametric study

The $i(E)$ curve of BDD electrode in 0.1M phosphate concentration (fig. 1b) shows an oxidation peak at potential $E = 0.9 \text{ V}$. This peak disappears in absence of phosphate ions in solution (fig.1a). The oxidation peak is therefore attributed to the presence in solution of phosphate ions. The back sweep doesn't show the reduction peak of the species formed during the oxidation process. The phosphate ions oxidation peak starts at a potential lower than water oxidation potential. This behaviour is not observed on a conventional electrode [29].

3.1.1.1. Phosphate concentration effect

The $i(E)$ curves of BDD electrode "fig. 2" are drawn at different phosphate ion concentrations. They show that the current oxidation increases with concentration in solution of phosphate ions. This confirms that the oxidation peak corresponds to phosphate ions oxidation.

3.1.1.2. pH solution effect

In order to get more information on phosphate ions oxidation process, investigations on the pH effect is very important. In fact, examination of figure 3 shows that phosphate ions oxidation is strongly dependent on the pH solution. Oxidation potential decreases when the pH increases. This shows that phosphate ions oxidation mechanism involves a proton exchange. Current oxidation is also more important at high pH value. This means that oxidation reaction is faster in a basic solution. According to the pH medium, the species that can be oxidized are PO_4^{3-} , HPO_4^{2-} or H_2PO_4^- .

3.1.1.3. Linear potential scan rate effect

The $i(E)$ curves recorded on BDD electrode at different potential

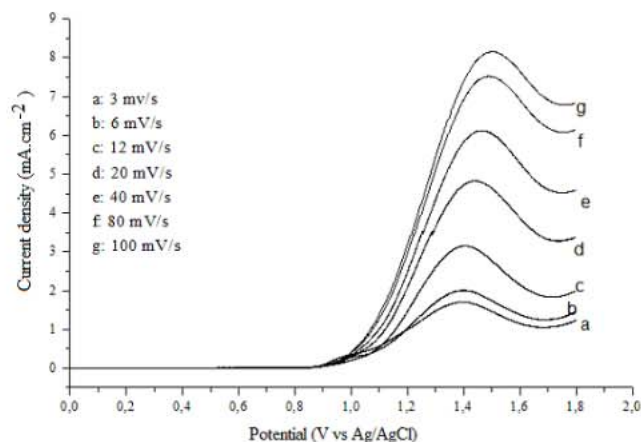


Figure 4. $i(E)$ curves of BDD at different potential scan rates: $[\text{PO}_4^{3-}] = 0.1 \text{ M}$; $\text{pH} = 12$.

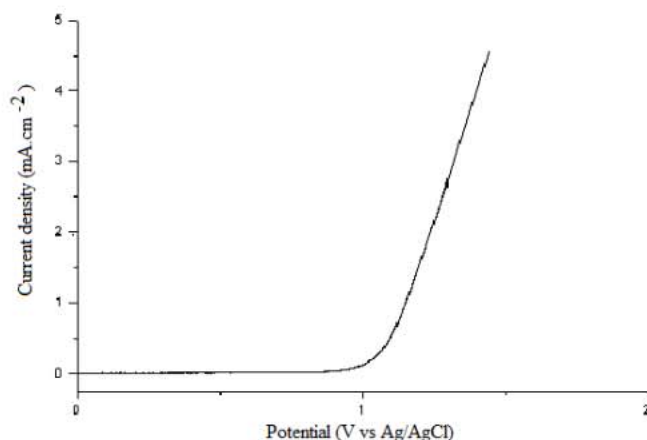


Figure 5. Linear sweep voltammetry curve of platinum electrode $[\text{PO}_4^{3-}] = 0.1 \text{ M}$; $\text{pH} = 12$; $v = 50 \text{ mV/s}$

scan rate (v) are reported in figure 4. They show that oxidation peak current intensity increases when the potential scan rate increases. After ohmic drop correction, figure 4 shows that the oxidation peak potential increases when the potential scan rate increases. This is in favour of an irreversible phosphate ions oxidation process on BDD.

3.1.2. Electrolysis experiments

After electrolysis on BDD of 0.1M phosphate ions solution at fixed potential ($E = 1.6 \text{ V}$), a quantitative analysis of the peroxodiphosphates using standard method [30] gives an evaluation of peroxodiphosphates ($\text{P}_2\text{O}_8^{4-}$) formed in anodic compartment. Phosphate ions oxidation on BDD electrode occurs with faradic yield of 80%. The same electrolysis experiment has been performed at the same physico-chemical conditions on a platinum electrode gives a faradic yield of 4%. Besides, the linear sweep voltammetry curve of platinum electrode (fig.5), drawn in the same conditions of BDD electrode, does not make up the oxidation peak of phosphate ions.

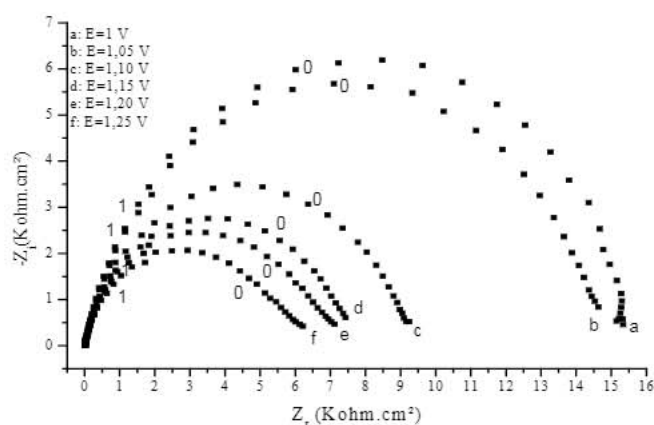


Figure 6. EIS diagram obtained on BDD at different potentials a- 1V; b- 1,05V; c- 1,10V; d- 1,15V; e- 1,20V; f- 1,25V; $[\text{PO}_4^{3-}] = 0,1\text{M}$ Logarithmic parameters frequency

Table 1. Characteristics of the EIS diagrams corresponding to figure 6

Potential (V)	R_c ($\text{k}\Omega.\text{cm}^2$)	Capacitance ($\mu\text{F}.\text{cm}^{-2}$)	Top frequency (Hz)
1.00	15,9	1,38	0,79
1.05	14,8	1,42	1
1.10	9,5	1,56	1,58
1.15	7,2	1,70	2
1.20	7,1	1,83	2,5
1.25	6,7	1,93	3,1

3.1.3. Electrochemical impedance spectroscopy (EIS) measurements

The impedance diagrams realized at different potentials corresponding to the oxidation domain of phosphate ions are presented on figure 6.

Examination of impedance diagram (Fig. 6-a) makes up a capacitive loop at high frequency domain and an inductive loop at low frequency domain. The inductive loop disappears when electrode potential increases (fig. 6-b, 6-c, 6-d, 6-e and 6-f). The R_c resistance associated to the capacitive loop decreases when the applied potential increases. The top frequency of capacitive loop and the deduced capacitance increase with the applied potential (table 1).

Impedance measurements, investigated at a fixed potential $E = 1,3\text{V}$ and at different rotating speeds (ω) of the electrode (fig.7), give approximately the same EIS diagrams.

3.2. Discussion

In the present study, voltametric measurements show that phosphate ions oxidation is possible on BDD before water oxidation. It isn't the case using a conventional electrode like platinum. Fichter and col. [31-33] have prepared with success a mixture of unstable peroxomonophosphate and stable peroxodiphosphate products. These authors proceeded by electrolysis of phosphate solution at a

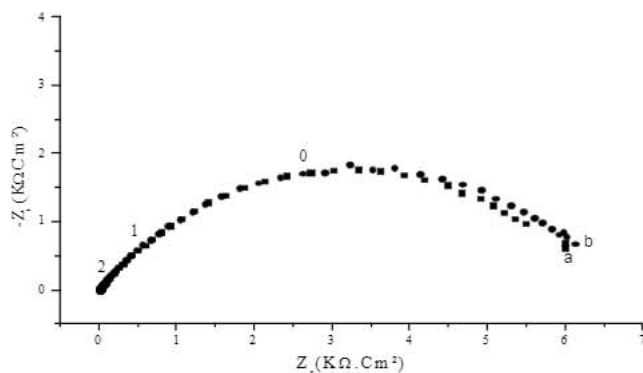


Figure 7. EIS diagrams of BDD electrode in the phosphate solution at different electrode rotating rate : a- $\omega = 1500$ rpm ; b- $\omega = 2000$ rpm; $[\text{PO}_4^{3-}] = 0,1\text{M}$; $E = 1,3\text{V}$
Logarithmic parameters frequency

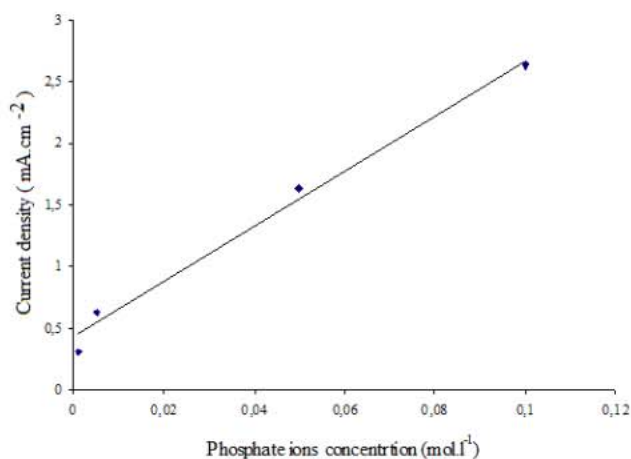


Figure 8. Oxidation current evolution with phosphate ions concentration.

low temperature and under weak current density using platinum electrode as anode and by adding reaction promoters. The obtained yield is about 30 to 80 % of peroxodiphosphate depending on the nature of used phosphate solution.

In the present study, it is shown that phosphate oxidation depends significantly on the pH solution (fig. 3). The reaction rate is enhanced in a basic environment. At high pH, current oxidation is more important. The oxidation potential evolution study shows that the oxidation process involves a proton exchange. M. A. Rodrigo and col. [22, 34] have synthesized peroxodiphosphate and peroxomonophosphate on BDD. They demonstrate that the oxidation yield is strongly dependant on pH, concentration and current intensity.

The linear dependence of oxidation current on phosphate ions concentration (fig.8) shows that BDD electrode could be used as indicator to phosphate ions content in solution. But more studies must be investigated in order to confirm its suitability.

On the other hand, at the low potential scan rate domain, the evolution of oxidation current with the square root of the potential scan rate presents a linear trend (Fig.9). But, at high potential scan

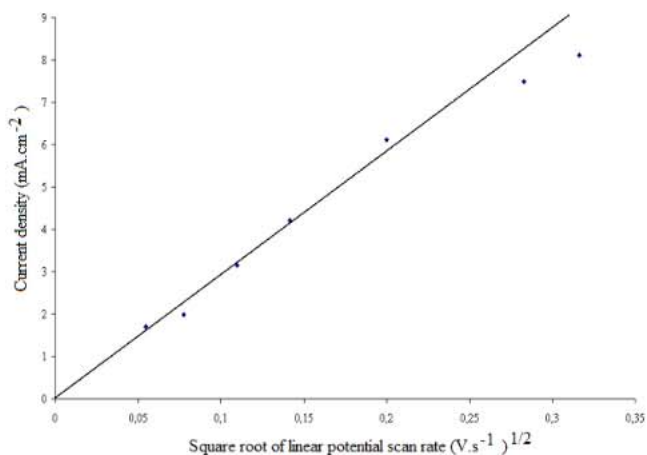
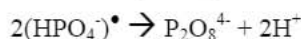
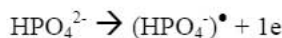
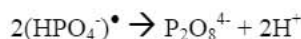
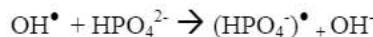


Figure 9. Evolution of current oxidation with square root of potential scan rate.

rate, a deviation from linearity occurs. This behaviour is attributed to adsorption phenomenon on electrode surface. This result is in good agreement with literature result [22, 34]. Indeed, it was indicated that the oxidation of phosphate ions to peroxodiphosphate takes place according to a radical mechanism. Generally, radical reactions happens using adsorbed species. The probable radicals species may be $(\text{PO}_4^{2-})^\bullet$, $(\text{HPO}_4^-)^\bullet$, $(\text{H}_2\text{PO}_4)^\bullet$ or OH^\bullet in relation to pH solution and electrolysis current [35]. In our case, the electrolysis tests occurred at fixed potential ($E = 1.6\text{V}$) and in basic mild ($\text{pH} = 12$). In this case, the oxidation reaction relates to mainly the transformation of HPO_4^{2-} species or $(\text{HPO}_4^-)^\bullet$ radical to peroxodiphosphate ions probably in accordance to the following mechanism:



At high current oxidation, electrolysis may lead also to OH^\bullet radical formation. This later contributes to phosphate oxidation process as follows:



This result is confirmed by the presence in solution of the peroxodiphosphate species after electrolysis at a fixed potential. This result is in a good agreement with the literature results [37]. It is suggested that the oxidation of ions HPO_4^{2-} to $\text{P}_2\text{O}_8^{4-}$ occurs according to a complex mechanism which makes up some radical species. The nature of radical species depends on current density and pH solution (like OH^\bullet , $(\text{H}_2\text{PO}_4)^\bullet$, $(\text{HPO}_4^-)^\bullet$...).

About EIS measurements, the value of the frequency at the top of the capacitive loop is relatively low. The corresponding phenomenon of relaxation cannot be attributed only to the charge transfer. The capacitance value associated to the capacitive loop is very low compared to the ordinary double layer capacitance value. Besides,

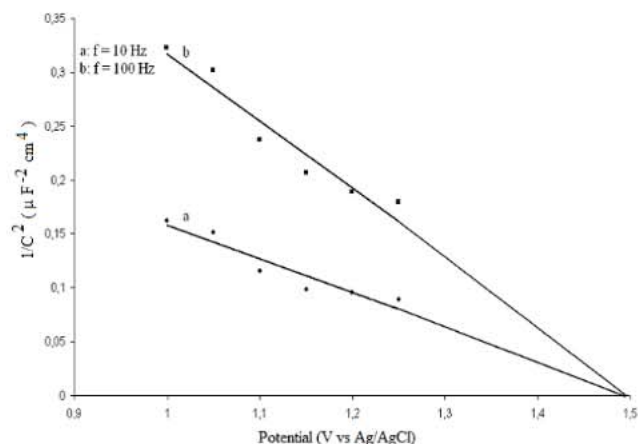


Figure 10. Mott Shottky plot corresponding to EIS diagram of figure 6

the impedance diagrams presented in figure 6 makes up that the capacitive loop corresponds to the superposition of several relaxation phenomenon (transfer, adsorption...). Moreover, this observation is clearly shown on EIS diagram of figure 6-a. This later makes up the beginning of an inductive loop at low frequency domain. The inductive loop can be attributed to adsorbed species on electrode surface. This result is compatible with the results of voltametric study related on figure 9 and with the observations cited in literature [22, 34].

The Mott Shottky plot of the capacitance associated with the capacitive loop, shows that the evolution of $1/C^2$ with electrode potential at two different frequencies (100 and 10 Hz) (fig.10) has a linear trend. The negative slopes of the straight lines indicate that the interface electrode-solution presents the behaviour of p-type semiconductor [36]. The flat band potential is $E_{FB} = 1.49$ V. This value is compatible with that given in literature for BDD electrode with similar doping [37].

4. CONCLUSION

In the present study, it is shown that phosphate ions oxidation on BDD electrode occurs before oxygen evolution. The effect of linear potential scan rate and of the effect of phosphate ions concentration make obvious that the oxidation process is very complex. The study of the dependence of the phosphate ions oxidation on BDD upon pH solution shows that oxidation reaction rate is enhanced at higher pH values and leads to peroxodiphosphate formation. The electrolysis experiments at pH = 12 showed that the product of the phosphate ions oxidation is peroxodiphosphate ($P_2O_8^{4-}$). The electrochemical phosphate oxidation on BDD occurs with a faradic yield of 80%.

EIS measurement reveals that oxidation mechanism happens following several steps with adsorbed radical species. The Mott Shottky plot indicates that the electrode-solution interface is similar to p-type semiconductor with flat band potential $E_{FB} = 1.49$ V.

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