A comparative study on the electrochemical production of H$_2$O$_2$ between BDD and graphite cathodes

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ABSTRACT

This work presents a comparison of the electrochemical production of hydrogen peroxide via the cathodic reduction of oxygen using two cathode materials of boron-doped diamond (BDD) and graphite. The effect of other operational parameters such as pH, applied current density ($j$), and support electrolyte concentration (ionic conductor media) on the generation of hydrogen peroxide was also investigated. The results indicate that highest hydrogen peroxide concentration is achieved when using graphite as cathode at pH = 3, $j =$ 0.25 mA cm$^{-2}$ and 0.05 M supporting electrolyte (Na$_2$SO$_4$) concentration. When using BDD, the conditions giving the best results in terms of accumulated H$_2$O$_2$ concentration were pH = 3, $j =$ 1.28 mA cm$^{-2}$ and 0.1 M supporting electrolyte concentration. It was concluded that in the studied range of variables graphite is better than BDD cathode regarding the amount of hydrogen peroxide electrochemically produced since nearly twice H$_2$O$_2$ was produced when using graphite than that obtained with BDD. Despite this, BDD was found to use current more efficiently at low applied potential. At the best operating conditions, the current efficiency for graphite cathode was 28% while for BDD was 89%.

INTRODUCTION

Water pollution has become more important and more difficult to deal with over time. This is mainly due to various pollutants being more abundant and persistent. Despite of the existence of water treatments, most of them are inefficient in terms of rate degradation and cost. In this sense, conventional wastewater treatment technologies such as biological degradation, physical or physicochemical processes do not always provide satisfactory results since they generate large volumes of sludge, thus causing secondary environmental problems [1]. Therefore it has become compulsory to develop more efficient processes that allow the pollutant degradation either to less harmful compounds or even better to their complete mineralization. In this context, advanced oxidation processes (AOP) are useful since they involve in the generation and use of strong transient oxidizing molecules. Among these molecules, special attention has been given to the radical OH• since is a powerful (E° = 2.8 V/SHE) [1], non-selective oxidant. This radical can be generated by the reaction of H$_2$O$_2$ with transition metals as shown in Eq. 1 [2], O$_3$ Eq. 2 [3,4] and UV light Eq. 3 [5].

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^\bullet + \text{OH}^- \quad (1)$$

$$\text{H}_2\text{O}_2 + 2\text{O}_3 \rightarrow 2\text{OH}^\bullet + 3\text{O}_2 \quad (2)$$

$$\text{H}_2\text{O}_2 \xrightarrow{\text{hv}} 2\text{OH}^\bullet \quad (3)$$

These processes have been extensively studied and have achieved high rates of degradation. To carry out the aforementioned processes, commercial hydrogen peroxide is usually employed. An alternative that is
worth evaluating, however, is the *in situ* production of H$_2$O$_2$ in aqueous medium by reducing dissolved molecular oxygen with 2e$^-$ at the cathode. In this sense, Wang et al. [6] have suggested that the following paths may occur: O$_2$ can be electrochemically reduced either directly to water without intermediate formation of H$_2$O$_2$ (called “direct” 4e$^-$ reduction) or towards H$_2$O$_2$ (called “series” 2e$^-$ reduction). The production of water also occurs through a 4e$^-$ sequential or “series” transfer pathway. There is first in this route with the transfer of 2e$^-$ to adsorbed molecular oxygen to form the adsorbed peroxide species. These species receive two more electrons to form water [6,7]. Thus, in summary, the produced peroxide can be electrochemically reduced to water, catalytically decomposed onto the electrode surface or desorbed into the bulk. This last process is depicted in Fig. 1 which also suggests the simultaneous production of hydrogen, which may occur in acidic media by means of Eq. 4 [7],

$$2H^+ + 2e^- \rightarrow H_2 \tag{4}$$

It is believed that this way of producing H$_2$O$_2$ is a sustainable process since it does not use toxic solvents. In addition, since H$_2$O$_2$ is continuously generated, hence, it eliminates transportation and storage costs. It also increases safety since it eliminates risky handling. Consequently, several investigations have been conducted into this subject and the variables that have received more attention are the electrode material, current density and pH. Within literature it can be found that the main studied electrodes are: gas diffusion electrode (pH = 3) [8-11] three dimensional felt [5], carbon sponge (pH = 2.8) [12], boron-doped diamond (BDD) cathode (pH = 3) [13,14], graphite-felt cathode (pH = 3) [15], carbon felt (pH = 3) [1,12,16], reticulated vitreous carbon (pH = 2.5, 6, 10) [17,18], graphite, activated carbon immobilized onto graphite surface and carbon nanotubes immobilized onto graphite surface (pH = 3) [19], PAN (polyacrylonitrile) based activated carbon fiber cloth [20]. Among these materials, the most promising ones are graphite and BDD. Both materials are stable to pressure and temperature, resistant to chemicals, but lifetime for graphite is shorter than BDD. The latter, however, is highly expensive and this still motivates the study of the H$_2$O$_2$ production with other less expensive materials.

BDD has been usually studied as anode [1,2,10,14], and only a few times this material has been investigated as cathode [13]. So, the reported results present the potential use of BDD as cathode also and motivate the comparison of its performance with other cathodic materials. Hence, this work aims to study the effect of pH, current density, support electrolyte concentration and electrodes material on the electrochemical production of H$_2$O$_2$.

**MATERIALS AND METHODS**

1. **Materials**

Hydrogen peroxide was produced by using either BDD or graphite electrodes. The geometric area for both BDD electrodes and graphite bar electrodes was 6.3 cm$^2$. Analytical grade sulphuric acid, sodium sulphate, sodium hydroxide, hydrogen peroxide (Fermont) and titanium IV oxide (Sigma) was employed. All solutions were prepared with deionized water obtained from a Millipore Direct Q3 UV equipment with resistivity >18 MΩ cm.

2. **Electrochemical System**

All experiments were carried out at laboratory scale in a 100 mL undivided cell. The experiments were performed at constant currents supplied by a DC power source (GWINSTEK GPR-1820HD). The intergap distance between electrodes was 2 cm. The experimental set up is depicted in Fig. 2.

The studied variables were electrode material, electrolyte concentration and current density. Their effect on the production of H$_2$O$_2$ was investigated. BDD and graphite were evaluated as electrode material. Sodium sulfate was used as supporting electrolyte and its effect was studied at two molarities, 0.05 and 0.1 M. Current density was investigated in the range of 0.03 to 0.38 mA cm$^{-2}$ for graphite.

Prior to electrolysis, air as source of oxygen was
bubbled through the system for 10 min. This time was
determined to be adequate to reach a steady oxygen
concentration in the solution before reaction. pH was
adjusted with a 0.1 M, 0.01 M H₂SO₄ or 0.5 M NaOH
solution. During electrolysis, air was continuously
sparged near the cathodic surface to ensure the
essential oxygen for the electrochemical reactions. The
solution was continuously stirred with a magnetic bar
to improve gas-liquid-solid mass transfer. Temperature
and dissolved oxygen were monitored by using a
HQ40d HACH meter of dissolved oxygen and the
pH solution was measured by a HI 9811 HANNA pH
meter.

3. Hydrogen Peroxide Concentration

Samples were withdrawn from the reactor at regular
time intervals and the concentration of accumulated
H₂O₂ was spectrophotometrically determined by
Ti(SO₄)₂ method (prepared from titanium IV oxide)
[21]. The absorbance of the treated solution was
measured using a UV-Vis spectrophotometer (HACH
DR 5000) at λ = 408 nm. The reported concentration
for each sample is the average of three measurements.

4. Voltammetry Study

Cyclic voltammetry was employed to confirm
hydrogen peroxide generation using a conventional
three-electrode cell coupled to a computer controlled
potentiostat Epsilon-BAS. The electrodes were BDD
or graphite as working electrodes, a platinum wire
as counter electrode and an Ag/AgCl electrode as
reference. Cyclic voltammograms were acquired at a
scan rate of 100 mV s⁻¹ at room temperature and were
recorded using a program of potential within the range
of 1.5 to -1.5 V, starting at the null-current potential (Eᵢ
= 0 V) vs Ag/AgCl in the anodic direction, inverting
the scan potential when the oxidation limit was reached
and at this point the cathodic scan was started.

RESULTS AND DISCUSSION

1. Graphite Cathode

1.1. Cyclic voltammetry study

Figure 3 shows the cyclic voltammetry of a working
solution in the presence and absence of oxygen (N₂
purging). It can be observed that O₂ presence exhibits
an evident current response at a peak current (Iₓ) of
\(-2.7 \times 10⁻²\) mA and a cathodic potential (Eₓ) of
-1.0 V vs Ag/AgCl. This peak is attributed to the generation of
hydrogen peroxide through oxygen reduction (Eq. 5)
[8] at a potential value close to that obtained with other
carbonaceous substrates [22].

\[ O₂ + 2H^+ + 2e^- \rightarrow H₂O₂ \quad (5) \]

1.2. Effect of current density

To determine the effect of applied current on the
electrochemical generation of H₂O₂ when using graphite
cathode, current density values of 0.03, 0.25 and 0.38
mA cm⁻² were applied (Fig. 4a). It can be observed that
the best applied current density in this system was 0.25
mA cm⁻² which yields the highest accumulated H₂O₂.
Two general regions are distinguished in this figure
when a current density of 0.38 mA cm⁻² is applied. The
first region demonstrates a linear correlation between
the amount of produced H₂O₂ and time up to 60 min.
After this point, the accumulation rate of H₂O₂ gradually
decreased and reached a plateau in the second region. This
plateau corresponds to the steady-state concentration
and can be explained by further oxidation of H₂O₂ on
the anode to produce intermediate H₂O₂ radicals by
Eqs. 6 and 7 [23] and also can undergo decomposition
to O₂ either on the anode (heterogenous process) or in
the medium (homogeneous process) by means of Eq.
8 [24].Thus, at the steady state H₂O₂ is simultaneously
formed and decomposed in the system at the same rate.
Thus, at potentials higher than 1.93 V the 4e⁻ reduction
of O₂ leading to the formation of H₂O (Eq. 9) begins
to compete with the formation of H₂O₂ (Eq. 5). Since
the applied potential is 2.44 V when a current density of
0.38 mA cm⁻² is applied, the competition of Reactions
6 and 9 may also be contributing to the observed
decreased in H₂O₂ generation with time. Reaction 9 is
expected to become more competitive with time since
oxygen concentration increases when Reaction 8 occurs
and this is favored by increasing applied potential and
H₂O₂ concentration. It is worth noticing that a steady
state was not reached when a current density of 0.25 mA
According to the results shown in Fig. 4a, the initial reaction rates for the electrochemical generation of H$_2$O$_2$ are $2.2 \times 10^{-6}$ and $2.1 \times 10^{-6}$ M min$^{-1}$, for 0.25 and 0.38 mA cm$^{-2}$, respectively. These values are smaller in one order of magnitude than that reported by Badellino et al. [18], $9.7 \times 10^{-5}$ M min$^{-1}$. This may be due to the use of a divided cell which eliminates the simultaneous consumption of H$_2$O. So, the initial H$_2$O$_2$ generation rate is not significantly affected by current density. As discussed before the effect of a high applied current density is observed with time and is detrimental rather than beneficial. Thus the current density of 0.25 mA cm$^{-2}$ was chosen to conduct all other subsequent experiments with the graphite cathode.

1.3. Effect of pH

Figure 4b plots the effect of pH on the accumulated H$_2$O$_2$. It is observed that pH 3 is the most favorable one for the production of hydrogen peroxide. This result was expected because the production of H$_2$O$_2$ according to Reaction 5 implies that certain proton concentration is desirable. There exists at pH 6 and 12 a deficient concentration of H$^+$ therefore the electrogeneration of H$_2$O$_2$ decreases due to the diminished proton concentration. This is in agreement with results previously reported [6]. This detrimental effect of pH is also consistent with initial reaction rates values ($2.2 \times 10^{-6}$ at pH 3, $1.9 \times 10^{-6}$ at pH 6 and $8.8 \times 10^{-7}$ M min$^{-1}$ at pH 12). This shows that an increase in pH has a negative effect on concentration of accumulated H$_2$O$_2$. The initial reaction rates at pH 3 and 6 are similar though. This suggests that the [H$^+$] concentration initially present at pH 6 is close to the minimum to initiate Reaction 5 but not to maintain it. Besides, hydrogen peroxide is also unstable in basic solution and may decompose to yield oxygen and water [25].

1.4. Effect of supporting electrolyte concentration

Figure 4c shows the effect of supporting electrolyte concentration. It was found that the hydrogen peroxide concentration was only 3% higher when using a 0.1 M solution as compared to 0.05 M solution. This difference is not significant and it can be concluded that increasing the sodium sulfate concentration from 0.05 to 0.1 M does not have a significant effect on the hydrogen peroxide generation. This is in concordance with that previously reported [19]. Therefore it was decided to carry out the rest of the experimentation using a concentration of 0.05 M.

2. BDD Cathode

2.1. Voltammetry study

Figure 5 shows the cyclic voltammogram obtained when a BDD electrode is used. This voltammogram is the evidence of hydrogen peroxide being produced with BDD electrodes. The $I_{pe}$ ($-3.41 \times 10^{-3}$ mA) characteristic of hydrogen peroxide production is observed at $E_{pe} = -0.80$ V vs Ag/AgCl.
2.2. Effect of current density

Figure 6 shows the effect of current density on the concentration of accumulated H$_2$O$_2$. It is observed that in all experiments the amount of H$_2$O$_2$ increases with time without reaching steady state. It can also be observed that up to 80 min a current density of 0.03 mA cm$^{-2}$ (E = 2.8 V) leads to a readily production of hydrogen peroxide. After this time, however, the hydrogen peroxide accumulation rate slows down and this can be ascribed to the further oxidation of H$_2$O$_2$ on the anode to produce intermediate HO$_2$• radicals via Eq. 6 or to its chemical decomposition into water and oxygen via Eq. 8 [24]. It is worth noticing that a slight increase on current density (i.e., 0.07 mA cm$^{-2}$) leads to a reduction on cumulative H$_2$O$_2$ concentration. This could seem contradictory since a higher potential (3 V) is being applied. However, the analysis of the results obtained at even higher current density (1.28 mA cm$^{-2}$, E = 6 V) suggest that higher applied potential changes the reaction route by which hydrogen peroxide is being produced. So, it seems that between 2.8 and 3 V there is an applied potential value where the anodic rather than the cathodic production of H$_2$O$_2$ is more likely to occur according to the following reaction sequence [26],

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{HO}^\bullet + e^- + \text{H}^+ \quad (10) \\
2\text{HO}^\bullet & \rightarrow \text{H}_2\text{O}_2 \quad (11) \\
(\text{H}_2\text{O}_2)^\text{electrode} & \rightarrow (\text{H}_2\text{O}_2)^\text{solution} \quad (12) \\
\text{H}_2\text{O}_2 & \rightarrow \text{O}_2 + 2e^- + 2\text{H}^+ \quad (13)
\end{align*}
\]

At this point it is not surprising why most of the existing literature regarding BDD for hydrogen peroxide production focuses on the use of BDD as anode rather than as cathode.

2.3. Effect of supporting electrolyte concentration

It is well known that the supporting electrolyte concentration has an important effect on electrochemical processes. Thus, experiments using 0.05 and 0.1 M solutions of Na$_2$SO$_4$ were performed using BDD as cathode to investigate the influence of this variable on the electrochemical generation of hydrogen peroxide. At the lowest concentration of sodium sulfate (0.05 M), hydrogen peroxide was not detected in the system and this is the reason for not including a graph with this variable. This fact means that H$_2$O$_2$ is not accumulated and its production cannot be disregarded though. It is plausible that H$_2$O$_2$ is simultaneously produced and consumed by Eqs. 5-8 since a higher voltage was applied in order to reach the desired current density due to the low electrical conductivity of the solution. This problem was overcome by using a higher concentration of supporting electrolyte. So, increasing the sodium sulfate concentration increases the electrogenerated accumulated amount of H$_2$O$_2$. This agrees with previous reports [11]. Therefore, a support
electrolyte concentration of 0.1 M was used to carry out all experiments with BDD as cathode.

3. Comparison of Graphite and BDD as Cathode Materials

In order to investigate the effect of cathode materials on the generation of \( \text{H}_2\text{O}_2 \), several experiments were carried out using either graphite or BDD as cathode. Figure 4a shows the \( \text{H}_2\text{O}_2 \) concentration after 180 min of electrolysis, 6.2, 9.5 and 0.17 mg L\(^{-1}\) \( \text{H}_2\text{O}_2 \) were electrogenerated with graphite cathode and supporting electrolyte concentration 0.05 M for 0.38, 0.24 and 0.03 mA cm\(^{-2}\), respectively, while Fig. 6 shows the \( \text{H}_2\text{O}_2 \) concentration after 180 min of electrolysis 4.3, 4.7 and 1.5 mg L\(^{-1}\) was generated with BDD cathode and supporting electrolyte concentration of 0.1 M for 0.03, 1.28 and 0.07 mA cm\(^{-2}\), respectively. For comparison purposes, the conditions at which the best results in terms of \( \text{H}_2\text{O}_2 \) concentration were achieved, were used to calculate the current efficiency (CE) for each material according to the following equation,

\[
\text{CE} = \frac{nFC_{\text{H}_2\text{O}_2}V}{\int idt} 100
\]

where \( n \) is the number of electrons involved in Reaction 5, \( F \) is Faraday constant (96500 C mol\(^{-1}\)e\(^{-}\)), \( C_{\text{H}_2\text{O}_2} \) is \( \text{H}_2\text{O}_2 \) molar concentration (M), \( V \) is the solution volume (L), \( i \) is the applied current (A) and \( t \) is production time (s). CE for graphite cathode was 28 and 89% for BDD cathode, at applied potentials of 1.93 and 2.8 V, respectively. These results indicate that despite a twice \( \text{H}_2\text{O}_2 \) being produced with graphite cathode, BDD is more efficient in terms of use of current. This is true only when a low potential is applied (2.8 V).

In the studied range of variables, graphite may produce a higher amount of \( \text{H}_2\text{O}_2 \) than BDD due to its higher surface area that is a consequence of its expected mesoporosity [19]. BDD electrodes do not possess this characteristic and thus the only available area for \( \text{O}_2 \) reduction is the geometrical area.

**CONCLUSIONS**

The effect of pH, current density, electrolyte concentration and cathode material (graphite and BDD) on the amount of hydrogen peroxide produced electrochemically was established. At pH 3, it yielded the highest accumulated concentration of \( \text{H}_2\text{O}_2 \) in either graphite or BDD electrode as cathode. Regarding current density and electrolyte concentration, however, it was found that the use of graphite electrode as cathode requires less current density (0.25 mA cm\(^{-2}\)) and lower electrolyte concentration (0.05 M) than the use of BDD to attain a higher concentration of accumulated \( \text{H}_2\text{O}_2 \) (9.5 mg L\(^{-1}\)) in the system. In the electrochemical production of \( \text{H}_2\text{O}_2 \) graphite outperforms BDD as cathode although BDD uses energy more efficiently at low applied potentials.

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