Electrochemical Synthesis of Peroxyacetic Acid using Conductive Diamond Electrodes

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Abstract

In this work, the synthesis of peroxyacetic acid and peroxyacetate salts by electrolysis with conductive-diamond anodes is described, using three different raw materials: ethanol, acetaldehyde and sodium acetate. Results show that peroxyacetic acid is produced at significant concentrations during the electrolyses of the three raw materials, although sodium acetate achieves the highest efficiency and, at the same time, the smallest carbon mineralization. Acetaldehyde behaves as a good raw material during a first stage but afterwards it catalyses the decomposition of peroxyacetate to the acetate anion. Moderate current densities and slightly alkaline pH seems to promote the synthesis of peroxyacetic acid and to restrain raw matter mineralization.

Keywords: Electrosynthesis, peroxyacetic acid, conductive diamond

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1. Introduction

Peroxyacetic acid (PAA), also known as peracetic acid, is an organic peroxide in which the carboxylic group of acetic acid (-COOH) is transformed into a peroxocarboxylic group (-COOOH). It is a strong oxidant ($E = 1.962 \text{ V vs SHE}$) with a reduction potential larger than those of well-known oxidants, such as chlorine or chlorine dioxide¹. Depending on operating conditions, the PAA can present bleaching and delignification properties². For this reason, the PAA is used as bleaching agent and in the industrial synthesis of epoxides^{2, 3}. It is a very effective oxidant in water treatment^{4, 5}. It is also used as a fowl sanitizer, and it is known to be a good disinfectant whose action is based on the hydroxyl radical. PAA is a more potent antimicrobial agent than hydrogen peroxide, being rapidly active at low concentrations against a wide spectrum of microorganisms⁶⁻⁸. Thus, it has been found that hydrogen peroxide required much larger doses than PAA for the same level of disinfection⁹.

PAA is commercially available in the form of a quaternary equilibrium mixture containing acetic acid, hydrogen peroxide, PAA, and water. It can be produced from acetic acid and also from acetaldehyde. The first process (eq 1) consists of the oxidation of acetic acid by means of hydrogen peroxide¹⁰⁻¹², catalysed by sulphuric acid. It requires long reaction times.

The second process uses acetaldehyde as raw matter. The oxidation of acetaldehyde with air or oxygen produces the initiation of the reaction by means of an acetyl radical

which forms the peroxide radical with oxygen. The reaction ends with PAA formation¹³ according to eq. 2.

However, the peroxyacetic acid can experience a homolysis of the peroxide group and become to acetic acid. In addition, it is supposed that peroxyacetic acid reacts with acetaldehyde giving α -hydroxyethylperacetate. Later, for a cyclical mechanism of transition, it dissociates itself in two molecules of acetic acid (eq. 3). Therefore, PAA can be the main product if the oxidation is realized in soft conditions, preferably without catalyst and in a solvent such as ethyl acetate.

In recent years, electrochemical oxidation with conductive-diamond anodes has become one of the most promising technologies in the treatment of industrial wastes polluted with organics¹⁴⁻²⁴ and in the electrosynthesis of oxidants²⁵⁻³³. Compared with other electrode materials, conductive-diamond has shown higher chemical and electrochemical stability as well as a higher current efficiency. In addition, the high overpotential for water electrolysis is one of the most important properties of conductive-diamond in the processing of aqueous solutions; its electrochemical window is sufficiently large to produce hydroxyl radicals with high efficiency³⁴, and this species seems to be directly involved in the oxidation mechanisms that occur on diamond surfaces. As a result, conductive-diamond electro-oxidation of waste is presently

considered as an advanced oxidation technology. The advantageous properties described above have led to great improvements (in both efficiency and electrode stability) in the use of conductive diamond in the electrosynthesis of oxidants. A number of recent studies have been published in which the generation of peroxodisulphates³⁵, peroxodiphosphate³¹, percarbonates³⁶, ferrates^{32, 33} and perchlorates²⁹ by electrochemical techniques are described. Significant improvements are reported as compared to more commonly used synthesis methods.

With this background in mind, the goal of the work described here was to investigate the feasibility of generating peroxyacetic acid and its salts by electrolyses with conductive-diamond electrodes. In an effort to achieve this aim, bench-scale electrolysis assays of different raw material solutions on conductive diamond anodes were carried out in order to characterize the mechanism of the process and to clarify the role of the most significant process parameters (pH and current density).

2. Experimental.

2.1. Analytical procedures. Acetate standard solutions were prepared by dissolving the appropriate amount of CH₃COONa in water. Peroxyacetic acid was determined by titration with Na₂S₂O₃. The titration is based on the next procedure³⁷: 4 ml of a 25% (v/v) H₂SO₄ solution were added to a 10 ml PAA sample. An excess of solid KI was added and the iodide was oxidized by PAA to brownish iodine, then it was titrated with 0.01 M Na₂S₂O₃ until only a pale brown color remained (eqs. 4 and 5). One drop of 1% (w/v) starch solution was added and the titration was continued until complete decolorization occurred.

To dismiss the other oxidants and hydrogen peroxide presence, it was carried out different analytical techniques such as gas chromatography and permanganate addition. Gas chromatographic analyses were carried out in a column SUPELCOWAX 10 (30 m x 0.25 mm) (macroporous particles with 0.25 μm diameter). Volume injection was set to 10 μL . To oxidize hydrogen peroxide, 0.02 M KMnO_4 solution was added until the color of the solution turned pale rose. Oxidant stability rules out the hydroxyl radicals, ozone and other unstable oxidants presence. Therefore the oxidant electrogenerated comes from the partial oxidation of raw material forming a peroxo group.

2.2. Electrochemical cell. The electrosynthesis was carried out in a double-compartment electrochemical flow cell. A cationic exchange membrane (STEREOM L-105) was used to separate the compartments. Diamond-based material was used as anode and stainless steel (AISI 304) as cathode. Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm^2 each and an electrode gap of 15 mm. Boron-doped diamond (BDD) films were provided by Adamant (Switzerland) and synthesised by the hot filament chemical vapour deposition technique (HF CVD) on single-crystal p-type Si <100> wafers (0.1 $\Omega\text{ cm}$, Siltronix). The anolyte and the catholyte were stored in dark glass tanks and circulated through the electrolytic cell by means of a centrifugal pump. A heat exchanger was used to maintain the temperature at the desired set point. The pH was monitored by means of the WTW-InoLab pHmeter.

2.3. Experimental Procedures. Bench scale electrolyses under galvanostatic conditions were carried out to determine the influence of the main parameters in the process. The anolyte and the catholyte consisted of 1 M solutions of ethanol (C₂H₆O), acetaldehyde (C₂H₄O) or sodium acetate (CH₃COONa). The range of current densities employed was 300 to 1000 A m⁻². The range of pH studied was 1 to 13.

3. Results and discussion.

Figure 1 shows the influence of the raw matter with the applied electric charge, on the production of PAA into the anodic chamber of a double compartment electrochemical cell equipped with conductive-diamond anodes. This Figure also shows the mineralization of carbon obtained during the same electrolyses. The experiments were carried out with three different organic raw materials (ethanol, acetaldehyde and sodium acetate in 1M aqueous solutions) at a current density of 300 A m⁻², regulating the temperature at 25°C during the process. As it can be observed, PAA can be obtained from the three species tested with a significant production rate (C₂H₆O: 0.061 mmol/Ah; C₂H₄O: 0.203 mmol/Ah; CH₃COONa: 0.033 mmol/Ah). However, acetate behaves as the best raw material, because it allows obtaining the best faradaic efficiencies in the production of PAA and, at the same time, it obtains the lower mineralization percentage. Initially, this can be easily interpreted in terms of the hydroxylation of the carboxylic group by means of hydroxyl radicals produced on the surface of the diamond surface (eq 6-9).

In this point, it is worth to mention that this process has been previously reported and extensively explained for the production of inorganic peroxosalts such as peroxosulphates and peroxophosphates, obtained from the electrolyses with diamond of sulphates or phosphates solutions^{25- 35}. In those cases, processes are directly related to the production of hydroxyl radicals (or, at least, significantly contributed), which produces the formation of radicals of the anions that in later stages yield the peroxyacid or peroxosalt (depending on the operation pH) as shown in eqs. 9-10 for peroxodisulphate, eqs. 11-12 for peroxodiphosphate and eqs. 11 and 13 for monoperoxophosphoric acid.

The greater mineralization obtained in the case of the acetaldehyde, and especially in the case of the ethanol, indicates the small selectivity of the conductive-diamond electrolyses towards the direct transformation of the hydroxyl and the aldehyde groups into the peroxocarboxylic one, by the direct attack of oxygenated groups in the organic molecules, and prevent against their use as raw materials.

At this point, it is interesting to observe the changes of the main intermediates found during electrolyses of ethanol and acetaldehyde (Figure 2). As it is shown, during ethanol electrolysis both acetaldehyde and acetic acid are produced, although the concentrations of acetic acid measured were very small. In addition, two other intermediates were also monitored during the electrolyses but their concentrations were negligible and they were not identified (they do not correspond to any C1 or C2 alcohols, acids or aldehydes).

The changes observed for the electrolyses of acetaldehyde are of a great interest, because initially this raw matter shows to be the most efficient in the electrochemical production of the organic peroxyacid, but the trend in the production of PAA meets a maximum and then, it decreases to finally meet a constant value. A possible explanation for such behaviour is the decomposition of PAA catalyzed by acetaldehyde (eq 14), because the plateau is obtained just in the moment in which acetaldehyde is completely depleted from solution.

At this respect, during the electrolyses of acetaldehyde, significant amounts of acetate and smaller concentrations of the two other intermediates were found. This supports the less efficient production of PAA at long reaction times.

Concerning the other raw matter studied, no intermediates were found by HPLC during the electrolyses of acetate solutions, indicating that mineralization and PAA formation

are the lone processes occurring in the anodic chamber of the electrochemical cell, and that acetate is the best choice as raw matter for PAA production.

Figure 3 shows the effect of the pH (range studied from 1 to 13) during the electrolyses of solutions containing 1 M CH_3COONa . Initially, the pH was expected to have a great influence on the species formed during the electrosynthesis, but surprisingly no intermediates different of PAA were detected during the electrolyses of acetate at any pH range. In addition, it can be observed that the effect is not very important on the PAA production (merely a small increase for both slightly alkaline pH and highly acidic pHs). However it is very significant for mineralization which it is promoted at strongly acidic and alkaline pHs. This advises against the use of extreme pHs in the synthesis of PAA and suggests to use slightly alkaline pHs (range from pH 7 to 10) in order to optimize the yield and simultaneously not promoting carbon mineralization.

Figure 4 shows the effect of the current density on the sodium acetate electrolysis. In these experiments, the pH is not regulated but simply monitored, and the temperature was maintained in 25°C . As it can be observed, the initial rate of the oxidants generation does not depend of the current density applied. However, from applied current charges around $10\text{-}15 \text{ A h dm}^{-3}$, there is a significant change in the slope (production rate of PAA) for the larger current densities, decreasing significantly the efficiency of the process (although the trend remains linear at any time). At the same time, the mineralization rate is maintained in every case in a very low value and it is not increased by the current density but just maintained (Figure 4b). This can only be explained in terms of the decomposition of PAA to yield oxygen and acetic acid, which seems to be promoted working under harder oxidation conditions.

4. Conclusions.

From this work the following conclusions can be drawn:

- Conductive-diamond electrolysis can be successfully used to synthesize PAA from sodium acetate, acetaldehyde and ethanol solutions, although the efficiency and the intermediates are largely affected by the choice of the raw matter.
- Sodium acetate is the best raw matter because its electrolysis does not promote carbon mineralization and yield merely PAA. Efficiency of the process improves working at current densities close to 300 A m^{-2} (enough to produce hydroxyl radicals in the electrolytic cell used). Concerning the pH, it does not affect significantly to the efficiency but it can be advised to work under slightly alkaline pHs in order optimize the yield and simultaneously not to promote carbon mineralization.
- Acetaldehyde seems to behave as a good raw matter for low applied current charges but a side reaction prevents against its use because of the decomposition of the PAA formed.
- Ethanol electrolysis yields many intermediates and promotes a high mineralization of carbon.

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Figure captions

Fig. 1. Variation of the PAA concentration (part a) and carbon mineralization (part b) during the electrolyses with BDD anodes (j 300 Am^{-2} , T 25°C) of three different raw materials: 1 M $\text{C}_2\text{H}_6\text{O}$ ($\blacktriangle$), 1 M $\text{C}_2\text{H}_4\text{O}$ ($\square$), 1 M CH_3COONa ($\blacklozenge$).

Fig. 2. Main intermediates found during the electrolyses with BDD anodes (j 300 Am^{-2} , T 35°C) of $\text{C}_2\text{H}_4\text{O}$ (part a) and $\text{C}_2\text{H}_6\text{O}$ (part b). $\circ$ acetic acid; $\square$ acetaldehyde; $\triangle$ ethanol; * non identified product 1; + non identified product 2

Fig. 3. Variation of oxidants concentration (part a) and carbon mineralization (part b) with pH during the electrolysis of CH_3COONa solutions at different current charge passed. (1 M CH_3COONa , j 300 Am^{-2} , T 25°C).

Fig. 4. Variation of oxidants concentration (part a) and total organic carbon (part b) with current density during the electrolysis of CH_3COONa solutions. ($\square$) 300 Am^{-2} , ($\blacksquare$) 600 Am^{-2} , ($\blacktriangle$) 1000 Am^{-2} (1 M CH_3COONa , T 25°C).

Figure 1

Figure 2

Figure 3

Figure 4