Improving the efficiency of carbon cloth for the electro-generation of H₂O₂: role of PTFE and carbon black loading

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Abstract

In this work, H₂O₂ is electro-generated in the cathodic compartment of a divided filter-press cell with a carbon cloth in the configuration of a gas diffusion electrode using air as oxygen source. The effect of Teflon[®] content was studied and it was found that the appropriate content is within the range of 10-20%. The production was greatly enhanced after the air-brushing deposition (and subsequent annealing) of simply 0.5 mg of carbon black. Higher additions clogged the pores and resulted counterproductive in terms of H₂O₂ generation. At a current density of 25 mA cm⁻², the production rate was 15 mg H₂O₂ h⁻¹ cm⁻² with a current efficiency close to 100%. Production rate increased with current density up to more than 40 mg H₂O₂ h⁻¹ cm⁻² at 87.5 mA cm⁻². The good performance and ease of preparation of this electrode make it an interesting alternative to generate hydrogen peroxide for Electro-Fenton processes.

Keywords: hydrogen peroxide, carbon cloth, PTFE loading, carbon black, air-brushing, gas diffusion electrode

1 Introduction

The hydrogen peroxide (H_2O_2) was firstly synthesized by Louis Jacques Thénard back in 1818 by reacting barium peroxide with nitric acid ¹. Today, this compound is produced on an industrial scale by the Anthraquinone process and approximately 4.5 million tonnes per year in 2014 of this compound were consumed worldwide ². Most of the production is employed as reagent in chemical synthesis, bleaching agent in paper or textile industry and environmental applications ^{3, 4}.

Regarding the latter, the hydrogen peroxide is used as a green oxidant for the destruction of organic and inorganic pollutants in water courses, since its decomposition only leads to water and oxygen ^{5, 6}. More interestingly, this compound can be activated via transition metals (Fe, Cu, Ti, (Eq.1)) ^{7, 8}, ozone ^{9, 10} (Eq. 2), or UV light ^{11, 12} (Eq.3), among others, to decompose mainly into hydroxyl radicals $\cdot OH$, a powerful oxidant which is able to non-selectively destroy most organics and organometallic pollutants until their complete mineralization into CO_2 , water and inorganic ions ^{6, 13}.

Since its implementation in 1945 by BASF, the hydrogen peroxide is manufactured almost exclusively (>95%) by the Anthraquinone process. Although the yield is high and the process is profitable on a large scale, it is energy-intensive and generates considerable volumes of wastes (particularly solvents). In addition, the product has to be transported from the manufacturing point to the end-user, posing a safety risk and increasing overall energy consumption and carbon footprint of the process ¹⁴. Therefore, hydrogen peroxide produced and supplied in this way entails a significant environmental impact in opposition with green chemistry principles ¹⁵.

An alternative for hydrogen peroxide production is via the two-electron oxygen reduction reaction (ORR) in neutral, basic or acid (Eq. 4) medium ^{16, 17}:

Electrochemical devices can be operated at ambient temperatures in small plants and require relatively low capital investment allowing its *in-situ* or decentralized production close to the point of consumption ¹⁸. This way, the issues related to transport, storage and handling of this hazardous chemical are avoided ¹⁹. The cornerstone of electrochemical devices in general, and for H₂O₂ generation in particular, is the selection of the appropriate electrode material that, ideally, should meet the following requirements ^{18, 20}:

- a) High activity, working at high current densities with minimum catalyst loading.
- b) High selectivity, promoting specifically the product of interest.
- c) High stability, maintain previous characteristics over a long period of time.
- d) Low cost, enabling economic viability of the process.
- e) Low environmental impact, ensuring a clean overall production.
- f) Use of renewable materials, avoiding the use of precious metals contributing to sustainable development.

Although different metals and amalgams such as Ti ²¹, Ag ²², Pt-Hg ²³ or Pd-Hg ¹⁸ have been investigated to promote the two-electron pathway, it does exist a general assumption that carbonaceous materials gather the most favorable characteristics (high selectivity and working current density, commercial availability, cost and environmental compatibility) for its use as cathodic materials in the electro-generation of hydrogen peroxide ^{19, 24}. In the literature, many different type of carbonaceous materials has been used including graphite ^{19, 25, 26}, carbon felt ^{19, 27, 28, 29}, carbon sponge ^{28, 30}, reticulated vitreous carbon ¹⁹ or carbon cloth ²⁸. A wide range of approaches have been reported for the enhancement of the production such as deposition of metals, ^{31, 32} recently graphene ^{33, 34}, electro ³⁵ or

chemical oxidation³⁶ of carbon surfaces and some others^{37, 38, 39, 40, 41}. Interestingly, those cathodes fabricated by combining carbonaceous materials and Teflon (polytetrafluoroethylene or PTFE) have achieved interesting results^{29, 42}. For example, Yu et al. reported an increase of one order of magnitude (40.3 vs. 472.9 mg H₂O₂ dm⁻³ after 60 min at 5 mA cm⁻²) using an unmodified carbon felt and a CB/PTFE-carbon felt, respectively²⁹

Apart from the cathode material, a key limiting factor in the efficiency of hydrogen peroxide via ORR is the low solubility of oxygen in water at room pressure^{26, 42}. Gas diffusion electrodes (GDEs) have been widely investigated to supply oxygen to the cathode minimizing mass transfer limitations^{43, 44, 45, 46, 47, 48}. In a simplified way, a gas diffusion electrode is a porous material composed of a catalytic layer and a gas diffusion layer. In electro-generation of H₂O₂, catalytic face is in contact with the electrolyte whereas gas diffusion is facing the air/oxygen chamber.

In this work, a commercial carbon cloth with different PTFE loadings is used as support to deposit unmodified particles of carbon black (CB) to create the catalytic layer. The efficiency in the production of hydrogen peroxide is then assessed in a divided filter-press electrolyzer using the aforementioned electrode in the configuration of a gas diffusion electrode (GDE).

2 Materials and methods

2.1 Materials

All tests were performed in a Milli-Q water solution with a concentration of Na₂SO₄ 0.05 M supplied by Panreac (Barcelona, España). The experiments of H₂O₂ generation were conducted, if not otherwise specified, in a divided filter-press flow-by cell at a typical current density of $j = 25 \text{ mA cm}^{-2}$. Na₂SO₄ 0.05 M without pH modification was selected as inert background electrolyte. The anolyte and the catholyte volume were 0.5 dm³ each

(1 dm³ in total). They were recirculated at a flow rate of $Q_{\text{anolyte}} = Q_{\text{catholyte}} = 28 \text{ dm}^3 \text{ h}^{-1}$. Air was supplied at $200 \text{ Nm}^3 \text{ h}^{-1}$.

2.2 Carbon black deposition by air-brushing

The catalytic ink was prepared by dispersing the CB (Vulcan XC72R) into isopropanol as solvent for 30 min in an ultrasound bath. After that, the ink was uniformly distributed along the carbon cloth (only in the face acting as catalytic layer) by means of an air-brush using nitrogen as carrier gas^{49, 50}. During this step, the carbon cloth is placed over a home-made hot plate at a constant temperature of 80 °C. In this way, the solvent is easily evaporated and the CB particles are effectively deposited onto the surface. Once achieved the desired weight increase, the carbon cloth is annealed at 300 °C for 1 h.

2.3 Hydrogen peroxide measurement

The hydrogen peroxide concentration was measured by the potassium titanium (IV) oxalate method⁵¹ according to standard DIN 38 409, part 15, DEV-18. The titanium solution was supplied by Fluka and the absorbance was determined at $\lambda = 407 \text{ nm}$ by means of an Agilent 300 Cary series UV-Vis spectrophotometer.

2.4 SEM images

The images of the surface were obtained by means of a Scanning Electron Microscope (SEM) FEI model QUANTA 250 working under low vacuum with a detector of secondary electrons (LFD) or a backscattered electrons detector (BSED) as indicated in each caption.

2.5 Experimental set-up

In this work, a divided parallel-plate flow-by cell with a gas diffusion cathode with an active area of $5 \times 4 \text{ cm}^2$ was used as electrochemical cell (Figure 1). The cathode materials are carbon cloths with different PTFE loadings prepared by dip coating (from 0 to 40% weight percentage) and a thickness of 0.4 mm supplied by the Fuel Cell Store. On its part,

an IrO₂-coated titanium electrode (Tianode, India) with an active area of 5 x 4 cm² was used as counter electrode. Cathodic and anodic compartments are separated by means of a cation exchange membrane Nafion 117®. The electrochemical cell is connected to a Delta Elektronika ES-030-5 DC power supply. The electrolyte solution is recirculated by two peristaltic pumps JP Selecta Percom N-M whereas air is supplied by a JP Selecta Vacuum-Sel (Barcelona, Spain). The air is introduced bottom-up in the air chamber (number 3 in Figure 1). The flow is forced to pass through the gas diffusion electrode by installing and adjusting a back pressure valve in the outlet connection of the air chamber. A schematic representation of the set-up is shown in Figure 1.

Figure 1. a) Experimental set-up used in this work, b) Electrochemical cell. 1) Support plates 2) Gaskets 3) Air chamber 4) Porous cathode 5) Titanium current collector 6) Cathodic chamber 7) Cationic membrane 8) Anodic chamber 9) Counter electrode

3 Results

3.1 Influence of PTFE loading

In the first stage of this work, carbon cloths with different PTFE loadings (0, 5, 10, 20, 30 and 40%) were studied since it is known that PTFE plays a crucial role in the performance and durability of GDEs⁵². The results are shown in Figure 2.

Figure 2. Hydrogen peroxide accumulation at 120 minutes of carbon cloths with different PTFE loadings. ■ [H₂O₂]; ▨ Forbidden areas. $j = 25 \text{ mA cm}^{-2}$; background electrolyte: Na₂SO₄ 0.05 M; natural pH; anolyte and catholyte volume 0.5 dm³ each, $Q_{\text{anolyte}} = Q_{\text{catholyte}} = 28 \text{ dm}^3 \text{ h}^{-1}$ and air flow = 200 Ndm³ h⁻¹

Firstly, 0% PTFE carbon cloths were tested. After a few moments of operation (20-30 min), water passed through the cathode to the adjacent compartment, resulting in the flooding of the air chamber and the leakage of the electrolyte. Thus, this material did not successfully work as GDE. The same result was obtained in the case of 5, 30 and 40% PTFE carbon cloths.

In the case of low PTFE content, the reason behind the failure of the cathode is thought to be the excessive wetting of the fibers of the carbon cloth that which eventually leads to water passing through them instead of through the pores where the pressure of the liquid flow can be compensated by pressure of the air flow.

On the other hand, the excessive permeability of the high PTFE-content cloths (30 and 40%) makes impossible for the air flow to compensate the water pressure along the entire surface of the cathode, also leading to the flooding of the air chamber. Carbon cloths with 10% and 20% with an intermedium degree of hydrophobicity worked perfectly well and separated both compartments effectively. These results are in agreement with other works in which the loadings of PTFE were within the same range as that found in the present work. As examples, Thiam et al. used 10% PTFE-carbon cloths as GDEs ⁵³; Forti et al. synthesized a GDE with 20% PTFE content ⁴⁵; Carneiro et al. used approximately 12% ⁵⁴ whereas Barros et al. fabricated an electrode with 20% PTFE ⁵⁵. Therefore, carbon cloths with 0, 5, 30 or 40% PTFE contents were found not adequate for its use as GDEs and represent a forbidden area, colored in grey in Figure 2, whereas 10 and 20% PTFE carbon cloths can be used as materials for the construction of GDEs.

Next, H₂O₂ was electro-generated using 10 and 20% PTFE carbon cloths as GDEs. Standard conditions were defined to compare efficiency of carbon cloths towards H₂O₂ generation (electrolyte Na₂SO₄ 0.05 M at $j = 25 \text{ mA cm}^{-2}$ and natural pH). As shown in Figure 3, H₂O₂ concentrations at 120 min are 35 and 45 mg H₂O₂ dm⁻³ for 10 and 20% PTFE carbon cloths, yielding very low current efficiencies of 2 and 3 %. The aforementioned results are in agreement with previous results in which the accumulation of H₂O₂ is low, generally in the order of dozens of ppm ^{26, 28, 29, 35}. Petrucci et al. found a decrease in the accumulation of H₂O₂ when increasing the current from 3 to 5 mA cm⁻² in graphite, from 5 to 7 mA cm⁻² in a CF and from 7 to 10 mA cm⁻² in a RVC indicating that the limiting current density is in the order of a few mA cm⁻² in plain carbonaceous materials ¹⁹. Applying higher than the limiting current could lead to the promotion of side reactions, resulting in a loss of efficiency in the process. Therefore, it seems that 25 mA cm⁻² is a value well above the limiting current density for PTFE-carbon cloths.

However, higher current densities have been previously applied in the electrochemical production of hydrogen peroxide using GDEs with good results. For example, Barros et al. applied 212 mA cm^{-2} in a GDE fabricated from CB (Printex L6) - PTFE by the hot-pressing method ⁵⁵. On its part, Kolyagin et al. applied 110 mA cm^{-2} in a CB (acetylene black) - PTFE cathode ⁵⁶, both using pure O_2 to feed the GDE. Panizza et. al. used a carbon-PTFE cathode in a system similar to the one in this study and obtained around 300 mg dm^{-3} of H_2O_2 after one hour of experiment working at 30 mA cm^{-2} in a divided cell using atmospheric air to feed the GDE ⁴⁷. Those results indicate that there was still room to improve the performance of the carbon cloths.

3.2 Effect of carbon black loading

It has been previously reported that for an important generation of hydrogen peroxide in carbonaceous materials, an adequate hydrophobicity/hydrophilicity ratio is to be maintained in the catalytic layer whereas a significant but not excessive hydrophobic nature is desired in the gas diffusion layer of GDEs ^{57, 58}. To improve the generation of hydrogen peroxide, in this work the electrode was modified by means of deposition of CB.

3.2.1 Deposition of carbon black

Carbon black is a general denomination of a wide family of high surface-area-to-volume carbonaceous powders. In this case, the type of CB used was the most common used for electro-catalytical applications, Vulcan XC72R ($250 \text{ m}^2 \text{ g}^{-1}$ and a conductivity of 2.77 S/cm ^{59, 60}). This way, the face in which CB is deposited act as catalyst layer whereas the unmodified is the gas diffusion layer. In a first attempt, 1.5 mg of CB per cm^2 were deposited in the carbon cloths which demonstrated viability in 3.1, i.e., 10 and 20% PTFE

loading and they were annealed at 300 °C for an hour. A comparison between the hydrogen peroxide electro-generated before and after the modification is shown in Figure 3.a.

Figure 3. a) Concentration – time curves of hydrogen peroxide accumulation using carbon cloths unmodified (● 10% PTFE; ○ 20% PTFE) and modified with CB (■ 10% PTFE + 1.5 $mg\ CB\ cm^{-2}$; □ 20% PTFE + 1.5 $mg\ CB\ cm^{-2}$ loading); b) Concentration – time curves of hydrogen peroxide accumulation using carbon cloths modified with different CB loadings (■ 0.5 $mg\ CB\ cm^{-2}$; ● 1.5 $mg\ CB\ cm^{-2}$; ◆ 2 $mg\ CB\ cm^{-2}$; ▲ 2.5 $mg\ CB\ cm^{-2}$). $j = 25\ mA\ cm^{-2}$; background electrolyte: $Na_2SO_4\ 0.05\ M$; natural pH anolyte and catholyte volume $0.5\ dm^3$ each; $Q_{anolyte} = Q_{catholyte} = 28\ dm^3\ h^{-1}$ and air flow = 200 $Ndm^3\ h^{-1}$.

The difference in H_2O_2 generation before and after the deposition is rather important. After 15 min, the concentration using the unmodified carbon cloths is approximately $20\ mg\ dm^{-3}$ whereas in the carbon cloths with the deposition of CB is as high as $130\ mg\ dm^{-3}$, leading to a difference in current efficiency of 13 vs. 83%. In the case of the unmodified, the concentration will increase only slightly with the electrolysis time, yielding 35 and 45 $mg\ dm^{-3}$ as showed before in Figure 2. In the case of modified carbon cloths, the

concentration increases up to 630 mg dm⁻³ (50% current efficiency) after 120 min of electrolysis. A similar effect was observed in previous works using carbon felt as support for the deposition of CB/PTFE^{29, 61, 62}.

However, the accumulation is not linear with time. Different side reactions can affect the accumulation of H₂O₂. Basically, H₂O₂ can undergo self-decomposition (Eq. 5 and 6, be oxidized in the anode (Eq. 7) or reduced in the cathode (Eq. 8) as widely discussed in bibliography^{19, 44, 47, 56, 63}.

Once the addition and further calcination of CB has demonstrated to be efficient, by increasing the accumulation of H₂O₂ in more than one order or magnitude, its loading was optimized. Since no evident improvement results from the utilization of 20% PTFE loading carbon cloth, the amount of CB was optimized on the basis of 10% PTFE loading carbon cloth. With this aim, different CB loadings were added within the range 0.5 – 2.5 mg cm⁻². Figure 3.b shows the accumulation of H₂O₂ using carbon cloths with different CB loadings.

The concentration-time curves show the same tendency regardless of the addition of loading of CB in the CC. However, significant differences can be observed in the concentration of H₂O₂. The concentrations at 15 min are 153, 130, 111 and 108 mg H₂O₂ dm⁻³ yielding current efficiencies of 97, 82, 70 and 68 % for the carbon cloths with 0.5, 1.5, 2 and 2.5 mg CB cm⁻², respectively. It means that the H₂O₂ can be generated

approximately at a rate of $15 \text{ mg h}^{-1} \text{ cm}^{-2}$ with a current efficiency close to 100% in the PTFE/carbon cloth with $0.5 \text{ mg CB cm}^{-2}$. At 120 min of electrolysis, the concentrations measured in the bulk were 832, 636, 479 and $260 \text{ mg H}_2\text{O}_2 \text{ dm}^{-3}$ for CB loadings of 0.5, 1.5, 2 and 2.5 mg cm^{-2} , respectively.

The improved electro-activity for hydrogen peroxide is attributed to the formation of a microporous, and partially hydrophobic, layer in which the formation of triple-phase (oxygen gas – electrolyte – electrode) contact points (TCPs) is promoted^{64, 65}. This way, the deposition of CB constitutes a suitable method to easily enhance electro-activity of commercially-available carbon cloths for H_2O_2 electro-generation.

Nevertheless, the efficiency gradually decreases with the addition of CB so, contrary to what may be expected, the best electro-generation rate is obtained with the carbon cloth containing the lowest CB loading, that is, 0.5 mg cm^{-2} . The explanation to this phenomena may be found in the surface of the modified electrode. It was observed under a scanning electron microscope (SEM), as shown in Figure 4. The carbon cloth presents a well-defined lattice structure in which the individual bare fibers are packed forming thicker wires that are knitted in the same way as a fabric and air can flow through the pores in between the wires.

Figure 4. Scanning electron microscope images of bare and modified carbon cloth.

After the modification, the surface substantially changes. The fibers of the carbon cloth are coated with a gradually thicker and rough crust of CB. This way, the surface area and porosity may be increased and so would do the number of TCPs for oxygen-reduction reaction, improving the efficiency of the process in comparison to the unmodified carbon cloth.

Nevertheless, the increasing addition of CB leads to a progressive covering of the surface. In fact, in the case of the cloth with $2.5 \text{ mg CB cm}^{-2}$, the surface is so clogged that air may find an important diffusion resistance and may not be equally distributed along the surface. In this way, at high CB loadings the supply of oxygen to the gas-liquid-solid interface is drastically reduced slowing down the overall kinetics of the electro-generation of H_2O_2 . Therefore, the deposition of CB in carbon cloth fiber is beneficial for the production of hydrogen peroxide but it has to be added in the right proportion so pores are not obstructed.

3.3 Effect of current density

All the previous experiments were conducted under standard conditions to compare the performance of the different materials on equal terms. Once selected the best PTFE and CB loading, next parameter to be studied is current density as it usually determines kinetics and efficiency in electrolytic processes and is intimately linked to the economics of the process. In general, at low current densities ($j_{\text{applied}} < j_{\text{limit}}$), current efficiency is higher but part of the capacity of the reactor is underused and longer electrolysis time/larger electrode areas are required for a given production. On the other hand, at high current densities ($j_{\text{applied}} > j_{\text{limit}}$), current efficiency decreases because part of it is wasted in side reactions and, therefore, the specific charge consumed increases ^{16, 29}.

Figure 5.a shows H_2O_2 concentration-time curves whereas Figure 5.b shows the current efficiency at 15 min and at a given applied electric charge of 1.5 Ah dm^{-3} for current densities within the range $25 - 87.5 \text{ mA cm}^{-2}$.

Figure 5. Influence of current density on hydrogen peroxide generation. a) Concentration curves: ■ 25 mA cm⁻² ● 50 mA cm⁻² ◆ 75 mA cm⁻² ▲ 87.5 mA cm⁻². b) Current efficiency at 15 min (■) and at 1.5 Ah dm⁻³ (□). Electrode material: 10% PTFE – 0.5 mg cm⁻² CB; background electrolyte: Na₂SO₄ 0.05 M; natural pH; anolyte and catholyte volume 0.5 dm³ each, $Q_{\text{anolyte}} = Q_{\text{catholyte}} = 28 \text{ dm}^3 \text{ h}^{-1}$ and air flow = 200 Ndm³ h⁻¹.

As can be observed in Figure 5.a, the production rate of hydrogen peroxide at 15 min increases with current density. Particularly, 15.8, 25.3, 35.0 and 41.1 mg H₂O₂ h⁻¹ cm⁻² were measured for 25, 50, 75 and 87.5 mA cm⁻², respectively, but with a concomitant decrease in current efficiency: 99, 80, 73 and 59 %. After longer electrolysis time, apparent production rates also increases with current density up to 75 mA cm⁻²: 11.67, 16.05, 21.45 and 20.45 mg H₂O₂ h⁻¹ cm⁻² at 90 min, respectively. The further increase up to 87.5 mA cm⁻² does not lead to a greater concentration of hydrogen peroxide.

It should be considered that an increase in current density implies both the availability of more electrons for parasitic reactions and higher cell voltages that shifts cathodic potential to more negative values. Both aspects together may result in the promotion of side reactions, such as the cathodic decomposition of hydrogen peroxide (Eq. 8), the four-

electron pathway (Eq. 9) or hydrogen evolution (Eq. 10)^{16, 46, 66}. Thus, the concentration or accumulation of H₂O₂ measured in the bulk is the difference between its generation and destruction rates.

The current efficiency was also compared in terms of the applied electric charge (Figure 5.b). For a fixed value of 1.5 Ah dm⁻³ (experimental time of 90, 45, 30 and 26 min for 25, 50, 75 and 87.5 mA cm⁻², respectively) current efficiency do not decreases markedly (80% at 25 mA cm⁻² vs 73 % at 87.5 mA cm⁻²) with current density at low applied electric charges. It means that oxygen can be selectively reduced to hydrogen peroxide with good efficiency in this cathodic material even at a high current density.

Interestingly, the *in-situ* electrochemical production of hydrogen peroxide is particularly attractive for the Electro-Fenton process. This technology have been studied for different application such as the regeneration of activated carbon⁶⁷, the cross-linking in polymers⁶⁸ but mainly for the elimination of organic pollutants in water courses^{24, 69, 70}. Ideally, in this process the hydrogen peroxide is not accumulated in the medium but catalytically decomposed into hydroxyl radicals (Eq. 1, 2 and 3), therefore avoiding the side reactions that destroy the hydrogen peroxide when it is present in the bulk at relatively high concentration. In this manner, this cathodic material can be used to produce H₂O₂ hydrogen peroxide *in-situ* needed for Electro-Fenton processes at a both high rate and current efficiency with commercially-available materials and using air as oxygen supply.

4 Conclusions

From the present work, the following conclusions can be drawn:

- Too low or too high PTFE loading make impossible the use of carbon clothes as GDEs being the best value 10%.

- Air-brushing plus annealing of Vulcan XC72R is an effective method to increase the electrochemical generation of H_2O_2 by using PTFE-carbon cloth.
- Simply small amounts (0.5 mg cm^{-2}) of Vulcan XC72R are required to greatly increase the production of hydrogen peroxide. Higher amounts were found to be counterproductive.
- Oxygen can be selectively reduced to hydrogen peroxide at high current density using Vulcan XC72R-PTFE/carbon cloths. After the application of 1.5 Ah dm^{-3} at 87.5 mA cm^{-2} , the current efficiency for H_2O_2 accumulation was 73% using air as oxygen supply.

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