

# Alkaline peroxide electroynthesis by oxygen reduction using an acid anolyte in a divided reactor with a three-dimensional rotating cylinder cathode and two-phase flow induced by centrifugal force

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## Abstract

**BACKGROUND:** This work analyses the performance of a batch electrochemical reactor with a three-dimensional rotating cylinder cathode for the synthesis of alkaline peroxide by reduction of  $O_2$  under 0.1 MPa (abs). The centrifugal force produces a radial co-current flow of the gas and liquid phases through the cathode achieving good mass-transfer conditions for the  $O_2$  reduction.

**RESULTS:** Galvanostatic experiments carried out during 2 h at 2 A (macrokinetic current density  $398 \text{ A m}^{-2}$ ),  $30^\circ \text{C}$  and 1000 rpm with  $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  as anolyte demonstrates that the cationic exchange membrane Nafion<sup>®</sup> 415 is an appropriate separator. However, a small decrease in the alkalinity of the cathodic compartment was observed. The use as anolyte of an equimolar solution of  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  ( $1 \text{ mol L}^{-1}$ ) maintains constant the total alkalinity of the cathodic solution. An experiment of 6 h yielded  $10.3 \text{ g L}^{-1} \text{ H}_2\text{O}_2$  concentration with 62.3% current efficiency and  $10.6 \text{ kWh kg}^{-1}$  specific energy consumption, using  $\text{Na}_2\text{SiO}_3$  as addition agent.

**CONCLUSION:** A divided electrochemical reactor using an acid anolyte and a three-dimensional rotating cylinder cathode with co-current oxygen and liquid flows represents a simple strategy for localized generation of peroxide solutions with low total alkalinity.

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**Keywords:** hydrogen peroxide; electrochemical reactor; three-dimensional electrode; oxygen reduction

## INTRODUCTION

The search for environmentally friendly oxidizing agents has prompted the development of new processes for the production of these substances. One of the chemical reagents that have been studied is hydrogen peroxide. This oxidizing agent has the advantage that its decomposition only produces water and oxygen, which avoids the generation of hazardous by-products. Hydrogen peroxide has been displacing some uses of chlorine-based chemicals in the paper and pulp industry, e.g. bleaching and brightening processes, which are usually carried out in the presence of caustic soda.<sup>1</sup> Today, several alternatives are available for its production,<sup>2</sup> but the chemical industry mainly synthesizes hydrogen peroxide via the anthraquinone process. However, the need to extract, purify, concentrate and stabilize  $\text{H}_2\text{O}_2$  solutions promotes the production of dilute solutions of alkaline peroxide by electrochemical reduction of oxygen.<sup>3</sup> Reviews of this procedure were given by Foller and Bombard<sup>1</sup> and Oloman.<sup>4</sup> Likewise, the applications of hydrogen peroxide in the pulp and paper industry require a mole ratio of sodium hydroxide to hydrogen peroxide ranging from 0.68 to about 0.94:1. The commercial Huron–Dow Process is intended for on-site production of dilute alkaline peroxide for direct use

in the pulp and paper industry. Nevertheless, it is necessary to blend the product with purchased hydrogen peroxide to achieve the proper ratio of caustic to hydrogen peroxide.<sup>5</sup> Thus, several attempts have been proposed to overcome this problem in order to satisfy the requirements of the pulp and paper industry, which are focussed to the developments of methods to remove the excess of sodium hydroxide from the electrolytic cell product. Likewise, it is important to examine its production in a variety of electrolytes, such as dilute alkaline solutions, stated in different practical cases.

Kastening and Schmitz<sup>6</sup> provided a method of preparing hydrogen peroxide by indirect electrolysis in an alkaline catholyte with

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an organic redox mediator and an acid anolyte. In a divided reactor, graphite or glass-type carbon served as cathode whereas the anode consisted of platinum. The peroxide produced by reduction of oxygen with the organic mediator is precipitated as alkaline earth metal peroxide, filtered off and withdrawn from the electrolyte solution, whereupon it is suspended in water, and hydrogen peroxide is formed by introducing an acid into the suspension.

The acid anolyte membrane process was pioneered by Occidental Research Corporation.<sup>7–9</sup> A three-compartment cell with a proprietary carbon gas-diffusion cathode, DSA<sup>®</sup> anode, and both an anionic and a cationic Nafion<sup>®</sup> 415 membrane was used.<sup>7,8</sup> An acid electrolyte was introduced between the anode and the cationic exchange membrane while a basic electrolyte is circulated between the cathode and the anionic exchange membrane. With this combination of electrolysis and electrodialysis, hydrogen peroxide in neutral, acidic or basic solutions is generated at the central compartment. However, the anionic membrane deteriorated after the experiments so new membranes were used for each case. Likewise, Clifford and Rogers<sup>10</sup> proposed the use of electrodialysis to decrease the concentration of hydroxyl ions for electrochemical generated alkaline peroxide solutions. Jasinski and Kuehn<sup>9</sup> reported good performance for a reactor with only two compartments separated by a cationic exchange membrane to produce hydrogen peroxide with an acidic anolyte.

Huron Tech Canada<sup>11</sup> disclosed a process combining the co-generation of ammonium persulfate in an acidic anolyte with the cathodic production of alkaline peroxide in an electrochemical reactor divided by a cationic exchange membrane. The transport ratio between ammonium and hydrogen ions through the membrane determines the ratio of alkalinity to hydrogen peroxide in the cathodic compartment, which on a molar basis lies between 0 and 2, by providing appropriate working conditions. Ammonia can be removed by bubbling an inert gas through the catholyte solution and its recycling to the anodic compartment.

Hillrichs *et al.*<sup>12</sup> proposed a process making an aqueous alkaline solution with an alkali hydroxide/H<sub>2</sub>O<sub>2</sub> mole ratio of 0.5 to 2.5. Their cell comprised a porous oxygen-diffusion cathode, a cationic exchange membrane, a DSA<sup>®</sup> or H<sub>2</sub>-diffusion anode. An aqueous solution of H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> was used as anolyte, which was circulated between the anodic compartment and a reservoir. Thus, to maintain constant the acidity and the sodium concentration in the anolyte two alternatives were implemented: (1) a fresh Na<sub>2</sub>SO<sub>4</sub> solution was supplied to the reservoir at the same volume rate as the anolyte was withdrawn; and (2) Na<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>SO<sub>3</sub> was supplied to the reservoir. Another proposed strategy in the same patent was the use of an intermediate chamber between the anodic and cathodic compartments. When, in the intermediate chamber, an anionic exchange membrane was placed in front of the anode, a solution of H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> was circulated between the intermediate chamber and the reservoir, as in the previous case, and a solution of sulfuric acid was produced as an additional product from the anodic compartment, whereas when a cationic exchange membrane was placed in front of the anode the catholyte was circulated through the intermediate chamber between both cationic exchange membranes and is withdrawn from the cell.

Drackett<sup>13</sup> proposed the production of hydrogen peroxide in an electrochemical reactor divided by a bipolar membrane, where using alkaline solutions in both compartments it was possible to achieve alkali hydroxide/H<sub>2</sub>O<sub>2</sub> mole ratios lower than 1.

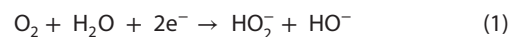
Likewise, the current efficiency during the generation of alkaline peroxide by electro-reduction of oxygen is affected either by the

homogeneous and heterogeneous decomposition of peroxide or by alternative reactions at the cathode. Sodium silicate is widely used as a peroxide stabilizer.<sup>14</sup> Other suitable stabilizing agents, such as stannates, phosphates and 8-hydroxyquinoline, are known.<sup>15</sup> Magnesium sulfate, calcium chloride, barium chloride, magnesium silicate, strontium nitrate, or their mixtures are also recognized as useful stabilizers against peroxide decomposition.<sup>10</sup> To avoid the catalyzed decomposition the use of ethylenediaminetetracetic acid,<sup>15</sup> diethylenetriaminepentacetic acid, triethanolamine or phosphate as complexing agents are proposed.<sup>16</sup> Additionally, Clifford *et al.*<sup>17</sup> suggested other organic compounds as stabilizing agents. Gyenge and Oloman<sup>18,19</sup> examined the influence of surfactants on the electro-reduction of oxygen, at pH below 12, and concluded that the cationic surfactant Aliquat<sup>®</sup> 336 at millimolar concentrations increases the current efficiency for hydrogen peroxide production. They proposed that an increase of the surface pH induced by the surfactant might be the cause for the enhanced oxygen reduction to hydrogen peroxide. Likewise, Gupta and Oloman<sup>20</sup> also added the non-ionic surfactant Makon<sup>®</sup> NF12 to the reactor feed to keep the separator wetted by the electrolyte.

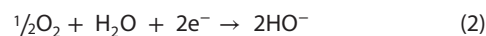
The rotating cylinder electrode is widely accepted in a number of interdisciplinary fields and its versatility has been fully demonstrated.<sup>21</sup> The aim of this study was to analyze the performance of a batch electrochemical reactor with a three-dimensional rotating cylinder electrode and two-phase flow induced by centrifugal force,<sup>22</sup> for the synthesis of alkaline peroxide using an acid anolyte to decrease the total alkalinity in the catholyte product, in comparison to that achieved with an alkaline anolyte.

## EXPERIMENTAL DETAILS

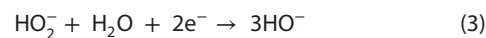
The desired cathodic reaction was:



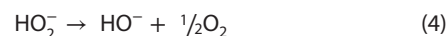
However, the following reactions can also take place at the cathode:



and



Likewise, in the bulk solution the catalytic decomposition of perhydroxide occurs according to:



The evolution of oxygen from an acid solution was the anodic reaction:

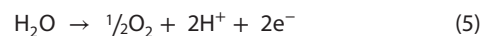
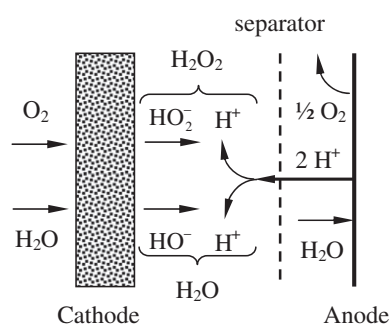
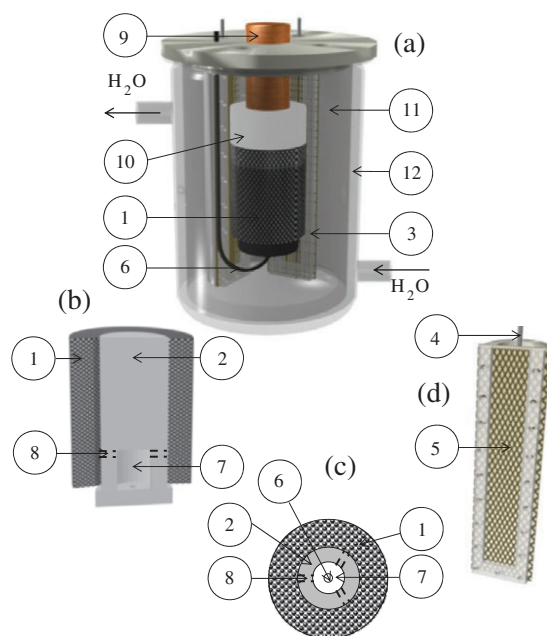


Figure 1 gives an outline of the expected reaction scheme using an acid anolyte, where the anodically generated hydrogen ions migrate through the separator and neutralize the products of the cathodic reaction. Then, in the case of an ideal behavior of the separator, characterized by only the migration of the hydrogen ions, the total alkalinity of the cathodic compartment must remain unchanged.

The experiments were performed in a batch reactor, 95 mm internal diameter and 140 mm high. The reactor was thermostated



**Figure 1.** Scheme of the expected reactions for the alkaline peroxide synthesis in an electrochemical reactor with an acid anolyte.



**Figure 2.** (a) Schematic representation of the electrochemical reactor. (b) View of the working electrode. (c) Bottom view of the working electrode. (d) View of an anodic compartment. 1, Three-dimensional structure; 2, graphite support; 3, anodic compartment; 4, anode; 5, window for the separator; 6, oxygen feeder; 7, oxygen chamber; 8, channels for oxygen distribution; 9, electrode shaft; 10, Teflon cylinder; 11, electrolyte container; 12, heating jacket.

by a heating jacket. The complete experimental arrangement is schematically depicted in Fig. 2a. The working electrode, Fig. 2b and c, was formed by a graphite cylinder, grade 6503 E Carbone Lorraine (Mersen, Buenos Aires, Argentina), 22 mm diameter and 44 mm long, which supports the three-dimensional electrode made of reticulated vitreous carbon (RVC), supplied by The Electrosynthesis Co., Inc. (Lancaster, NY, USA). Three ring-shaped discs, 22 mm internal diameter, 42 mm external diameter and 12.7 mm high were placed on the cylindrical graphite support to conform the three-dimensional electrode. The discs were cut from a 100 ppi (nominal pores per linear inch), RVC tile using a hollow cylindrical brass, cork-boring tool. The three-dimensional material was fixed to the support by graphite paint, which enhances the electrode conductivity. The bed depth of the three-dimensional structure in the direction of the current flow was 10 mm to ensure that the whole bed was working under limiting current conditions, as was previously calculated.<sup>22</sup>

The upper end of the cylindrical graphite support was attached to the motor shaft. The rotating reticulated vitreous carbon cylinder acts as a pump, drawing liquid from the bottom of the cell to the top.<sup>23</sup> Oxygen was fed at 0.1 MPa (abs) into a chamber inside the graphite cylinder, via a port located at its lower end, and it flows through the three-dimensional electrode by three radial channels symmetrically drilled in the support. Thus, the rotation of the electrode enables a co-current flow of the liquid and gas phases in radial direction, giving an appropriate intermixing between both. The oxygen volumetric flow rate, controlled with a gas pressure regulator, was  $9.36 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$  measured under ambient conditions and it was also bubbled in the solution 1 h before the experiment to ensure that the electrolyte is saturated with oxygen. For a total current of 2 A, the theoretical fractional conversion of oxygen according to Eqn (1) is 2.75%. Therefore, the feed of oxygen is in excess of the stoichiometric quantity. In a previous study,<sup>22</sup> the liquid volumetric flow rate at 1000 rpm rotation speed was calculated as  $1 \times 10^{-3} \text{ m}^3 \text{ s}^{-1}$ , which is higher than the gas volumetric flow rate. Then, it is expected that the hydrodynamic behavior of the reactor, the mass-transfer and the ohmic drop in the solution phase will be hardly influenced by the gas phase. Likewise, the high values of liquid volumetric flow rate associated with the turbulence promoting action of the reticulated structure produces good mass-transfer conditions for the reduction of dissolved oxygen, which is continuously replenished by the co-current gas flow.

Four platinum wires, 1 mm diameter and 140 mm long, were used as anodes with a total active surface area of approximately  $12 \text{ cm}^2$ . Each of them was put into an anodic compartment (Fig. 2d), made from a hollow hemi-cylindrical Teflon holder. The open face of the holder supports the separator fixed by a Teflon flange with silicone gaskets. Nafion<sup>®</sup> cationic exchange membranes and a microporous PVC diaphragm were used as separators. The volume of each anolyte was  $25 \text{ cm}^3$  and the separator area was  $21 \text{ cm}^2$ . The anodic compartments were placed symmetrically around the rotating electrode. Then, taking into account that the cathodic reaction is under mass-transfer control a uniform tertiary current distribution can be assumed. The gap between the external surface of the RVC working electrode and the separator was 5 mm and each platinum anode was placed near the separator. In the cathodic compartment  $0.5\text{--}2.5 \text{ mol L}^{-1}$  NaOH was used as the electrolyte and as anolyte  $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  or an equimolar solution of  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ ,  $1 \text{ mol L}^{-1}$ , which was frequently replenished with fresh solution to maintain the concentration and to avoid accumulation of the oxygen evolved at the anode. The electrolyte volume in the cathodic compartment was 0.45 L and 0.1 L in the anodic part.

The reactor was galvanostatically operated at 2 A,  $30^\circ \text{C}$  and 1000 rpm, unless otherwise indicated. The corresponding value of current density is  $398 \text{ A m}^{-2}$  external RVC area or  $522 \text{ A m}^{-3}$  electrode volume. At the end of the experiment, a sample of the solution was taken from the cathodic compartment, the  $\text{H}_2\text{O}_2$  concentration and total alkalinity as NaOH were separately determined by titrating the solution with  $\text{KMnO}_4$  and potassium biphthalate, respectively.<sup>24</sup> The stability of the alkaline peroxide generated in the catholyte was determined at room conditions by titrating an aged sample of a peroxide solution stored in a brown glass bottle isolated from light, heat and mechanical agitation. The half life,  $t_{1/2}$ , was determined according to:

$$t_{1/2} = \frac{t \ln 2}{\ln [C(0)/C(t)]} \quad (6)$$

where  $t$  is time (h) and  $C$  is concentration ( $\text{g L}^{-1}$ ).

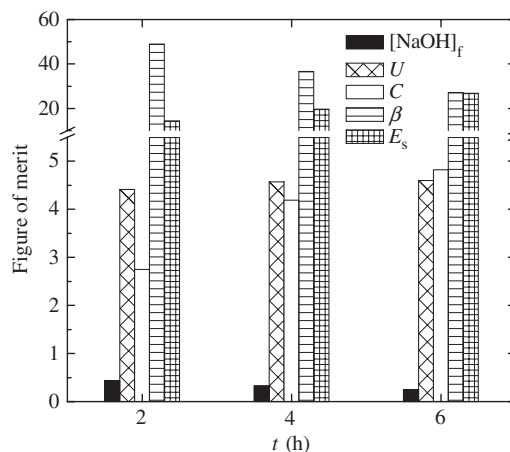
**Table 1.** Effect of separator material and initial NaOH concentration on the reactor performance

Separator	[NaOH] <sub>i</sub> (mol L <sup>-1</sup> )	[NaOH] <sub>f</sub> (mol L <sup>-1</sup> )	U (V)	C (g L <sup>-1</sup> )	β (%)	E <sub>s</sub> (kWh kg <sup>-1</sup> )
Microporous PVC	0.50	0.28 ± 0.06	4.74 ± 0.05	2.8 ± 0.3	49 ± 4	15.3 ± 1.2
	1.00	0.69	4.27	2.99	55	12
	2.01	1.62	4.23	3.05	54	12
Nafion® 415	0.50	0.44 ± 0.01	4.41 ± 0.07	2.75 ± 0.25	49 ± 4	14.3 ± 0.9
	1.00	0.91 ± 0.03	4.3 ± 0.1	4.3 ± 0.1	52 ± 3	13 ± 1
	2.00	1.85 ± 0.05	4.2 ± 0.2	1.6 ± 0.2	30 ± 5	23 ± 5
	2.54	2.42	4.22	1.5	27	24

Anolyte composition: [H<sub>2</sub>SO<sub>4</sub>] = 1 mol L<sup>-1</sup>; total current, *I* = 2 A; time, *t* = 2 h; rotation speed, ω = 1000 rpm; temperature, *T* = 30 °C. *U*, cell voltage; *C*, concentration; β, current efficiency; *E<sub>s</sub>*, specific energy consumption.

## RESULTS AND DISCUSSION

To corroborate our previous results, obtained with a similar reactor,<sup>22</sup> a preliminary experiment was made using a solution 2 mol L<sup>-1</sup> NaOH in the anodic compartment and 0.5 mol L<sup>-1</sup> NaOH as starting solution for the catholyte. Comparable values of peroxide concentration and current efficiency were measured and, as expected, the final total alkalinity was 0.81 mol L<sup>-1</sup>. However, lower values of cell voltage (2.96 V) and specific energy consumption (6.28 kWh kg<sup>-1</sup>) were achieved as a consequence of the small inter-electrode gap and the different configuration of the anodic compartments in the present reactor. The reactor performance varying the separator material and initial NaOH concentration is summarized in Table 1 for 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> as anolyte, where the cell voltage and the specific energy consumption correspond to average values, whereas the total alkalinity and the concentration of peroxide were measured in the final catholyte, which was used to calculate the current efficiency. The separators appeared stable and virtually unchanged and they were reused in all the experiments. Table 1 shows a similar behavior for both separators at low NaOH concentrations. However, an important decrease of alkalinity is observed when microporous PVC was used, which can be attributed to the diffusion of the components of both solutions by virtue of the concentration gradients. Then, the use of microporous PVC is inappropriate due to: (1) the catholyte product being contaminated by the anodic solution, and (2) a decrease in the total alkalinity increases the catholyte resistivity increasing the cell voltage, mainly in prolonged experiments. On the other hand, the cathodic compartment showed a lower decrease in total alkalinity when a cationic exchange membrane Nafion® 415 was used as separator. Taking into account reactions 1, 2 and 5 and that the current transport through a cationic exchange membrane should only be the result of migration of hydrogen ions, no change in the total alkalinity of the cathodic compartment is expected. According to Table 1, the best results were obtained for NaOH concentrations ranging from 0.5 to 1 mol L<sup>-1</sup>, where the highest hydrogen peroxide concentration and current efficiency were obtained with a low value in the specific energy consumption. However, it is inferred that 0.5 mol L<sup>-1</sup> NaOH becomes attractive in order to achieve a low value of the ratio between sodium hydroxide to hydrogen peroxide. Under these working conditions the electrochemical and rotational power requirements were 8.7 and 2.3 W, respectively. Figure 3 reports the figures of merit of the reactor as a function of the electrolysis time using as separator the cationic exchange membrane Nafion® 415. It can be observed that the hydrogen peroxide concentration approaches 4.8 g L<sup>-1</sup> when the electrolysis time is increased with a decrease in the



**Figure 3.** Figures of merit as a function of the electrolysis time. Separator: Nafion® 415, *I* = 2 A, *T* = 30 °C, rotation speed (ω) = 1000 rpm; initial anolyte: 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; initial catholyte: 0.5 mol L<sup>-1</sup> NaOH.

current efficiency. However, a diminution in the total alkalinity in the cathodic compartment is detected. At all times small values of sulfate concentration, in the order of  $1 \times 10^{-3}$  mol L<sup>-1</sup>, in the catholyte were measured spectrophotometrically.<sup>25</sup> Thus, the diffusion of sulfuric acid from the anolyte to the catholyte through the cationic exchange membrane can be disregarded. Moreover, the hydrogen peroxide concentration in the anolyte was very small, approximately 30–40 mg L<sup>-1</sup>. Thus, a cationic exchange membrane as separator is more effective than the microporous PVC because the membrane hinders diffusion of the species between both compartments avoiding contamination. However, the diminution of the number of moles of hydroxyl ions in the catholyte was the same as the decrease of hydrogen ions in the anolyte, which was volumetrically determined. Then, the exchange of these ions across the membrane because of the high water content of the polymer explains the non-ideality of the membrane. Further experiments were made using a bilayer membrane such as the Nafion® 900 series with carboxylic acid functionality to improve anion rejection, which showed an inappropriate behavior characterized by a high cell voltage as a result of the carboxylic acid functionality readily protonating.<sup>1,26</sup>

Table 2 shows the effect of the anolyte composition on the reactor performance. A Nafion® 415 cationic exchange membrane was used as separator. The use of an equimolar solution of Na<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> as anolyte allows current transport through the membrane to be performed by both hydrogen and sodium ions, which



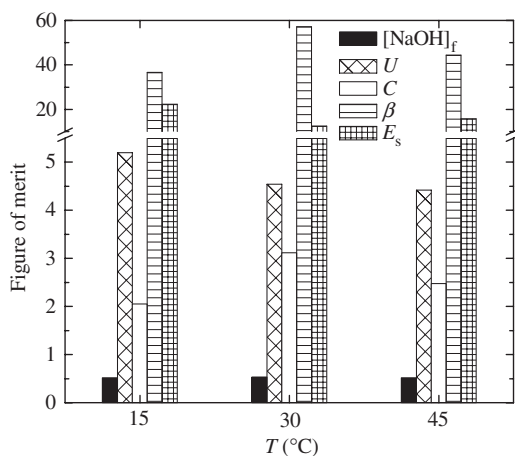
**Table 2.** Effect of anolyte composition

[NaOH] <sub>i</sub> (mol L <sup>-1</sup> )	Anolyte composition	[NaOH] <sub>f</sub> (M)	U (V)	C (g L <sup>-1</sup> )	β (%)	E <sub>s</sub> (kWh kg <sup>-1</sup> )
0.5	0, 1	0.44 ± 0.01	4.41 ± 0.07	2.75 ± 0.25	49 ± 4	14.3 ± 0.9
	1, 1	0.53	4.54	3.12	57	12.5
1.0	0, 1	0.91 ± 0.03	4.3 ± 0.1	4.3 ± 0.1	52 ± 3	13 ± 1
	1, 1	1.03	4.66	2.61	47	15.6

Separator: Nafion® 415, total current,  $I = 2$  A; time,  $t = 2$  h; rotation speed,  $\omega = 1000$  rpm; temperature,  $T = 30$  °C.

Anolyte composition is given as [Na<sub>2</sub>SO<sub>4</sub>] (mol L<sup>-1</sup>), [H<sub>2</sub>SO<sub>4</sub>] (mol L<sup>-1</sup>).

U, cell voltage; C, concentration; β, current efficiency; E<sub>s</sub>, specific energy consumption.



**Figure 4.** Figures of merit as a function of temperature. Separator: Nafion® 415,  $I = 2$  A,  $t = 2$  h, rotation speed ( $\omega$ ) = 1000 rpm; anolyte: 1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> and 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; initial catholyte: 0.5 mol L<sup>-1</sup> NaOH.

diminishes the migration of hydrogen ions. Thus, it is observed that the total alkalinity in the cathodic compartment is maintained approximately constant. However, the use of this anolyte requires that the electrolyte in the anodic compartment must be frequently changed to maintain constant concentrations of both hydrogen and sodium ions. A slight improvement is also observed in the other figures of merit of the reactor with 0.5 mol L<sup>-1</sup> NaOH initial concentration in the catholyte when Na<sub>2</sub>SO<sub>4</sub> was added at the anolyte.

The effect of temperature is summarized in Fig. 4. The working conditions in these experiments were: separator: Nafion® 415, anolyte: 1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> and 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, and 0.5 mol L<sup>-1</sup> NaOH as initial catholyte. It is observed that the total alkalinity remains constant in all experiments. The increase of temperature has two opposite effects: the first to enhance the mass-transfer and the second to decrease the oxygen solubility. So the appropriate operating value is a compromise between these and thus the more convenient temperature is 30 °C, where the lowest specific energy consumption is achieved giving the highest values of peroxide concentration and current efficiency.

Table 3 compares the results of experiments performed over 6 h with and without the addition of Na<sub>2</sub>SiO<sub>3</sub>; little influence on the current efficiency is observed. This can be attributed to the higher value of the hydrogen peroxide concentration due to this added reagent delaying auto-decomposition (reaction 4) corroborated by the higher value in the half-life as shown in Table 4. Additional experiments were carried out using as catholyte, 0.5 mol L<sup>-1</sup> NaOH with  $1.5 \times 10^{-3}$  mol L<sup>-1</sup> of either Aliquat® 336 or Triton® X-100. No

**Table 3.** Effect of Na<sub>2</sub>SiO<sub>3</sub> as the added reagent in the catholyte

Additive in catholyte	[NaOH] <sub>f</sub> (mol L <sup>-1</sup> )	U (V)	C (g L <sup>-1</sup> )	β (%)	E <sub>s</sub> (kWh kg <sup>-1</sup> )
None	0.62	4.14	9.8	61	11
Na <sub>2</sub> SiO <sub>3</sub> , 3 g L <sup>-1</sup>	0.65	4.19	10.3	62	11

Separator: Nafion® 415, [NaOH]<sub>i</sub> = 1 mol L<sup>-1</sup>, anolyte composition: [H<sub>2</sub>SO<sub>4</sub>] = 1 mol L<sup>-1</sup>; total current,  $I = 2$  A; time,  $t = 6$  h; rotation speed,  $\omega = 1000$  rpm; temperature,  $T = 30$  °C.

U, cell voltage; C, concentration; β, current efficiency; E<sub>s</sub>, specific energy consumption.

**Table 4.** Half-life ( $t_{1/2}$ ) of alkaline peroxide in different solutions

[NaOH] (mol L <sup>-1</sup> )	Addition agent	t (h)	C(0) (g L <sup>-1</sup> )	C(t) (g L <sup>-1</sup> )	$t_{1/2}$ (h)
0.45	None	19	2.52	1.95	104
0.92	None	24	2.93	2.50	107
0.65	Na <sub>2</sub> SiO <sub>3</sub> , 3 g L <sup>-1</sup>	23	10.32	9.16	134
0.45	Aliquat® 336, $1.5 \times 10^{-3}$ mol L <sup>-1</sup>	24.75	2.03	1.84	180

C, concentration; t, time.

improvement in the reactor performance was achieved with the use of these surfactants. However, it was observed that Aliquat® 336 enhances the half-life of hydrogen peroxide solutions as shown in the last row of Table 4.

The specific energy consumption reported in Tables 1–3 are higher than those previously given with an alkaline anolyte,<sup>22</sup> mainly due to the potential difference across the membrane, caused by the pH change on either side, increasing the cell voltage. According to thermodynamics, this pH gradient contributes 0.84 V to the cell voltage. However, an acid anolyte presents as advantage to obtain peroxide solutions with low total alkalinity in comparison with an alkaline anolyte.

Foller and Bombard<sup>1</sup> reported current efficiencies close to 90% to obtain 6 wt% H<sub>2</sub>O<sub>2</sub> with a mole ratio of 1.2:1 NaOH to H<sub>2</sub>O<sub>2</sub>, using a membrane process with an acid anolyte. These results are better than those reported in Tables 1–3. However, the batch reactor examined in the present contribution can be considered as a simple alternative for the on-site manufacture of alkaline peroxide, which has gained increasing attention because of the cost and the hazards associated with the transport and handling

of commercial concentrated  $\text{H}_2\text{O}_2$ .<sup>27</sup> Hence, these results open ways for improving cell design and exploitation conditions of electrochemical reactors for alkaline peroxide synthesis.

## CONCLUSIONS

- The concept of a three-dimensional rotating cylinder cathode and two-phase flow induced by centrifugal force was applied for the synthesis of alkaline peroxide via the reduction of oxygen with an acid anolyte using a divided electrochemical reactor.
- High current efficiency and low specific energy consumption were achieved using  $0.5 \text{ mol L}^{-1}$  NaOH as catholyte and a cationic exchange membrane, Nafion<sup>®</sup> 415, as separator. Alkaline peroxide was produced with low diminution of the total alkalinity in the catholyte when  $1 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  was used as anolyte. Microporous PVC as separator was ineffective in hindering the diffusion of species between both compartments.
- The use of an acid anolyte with the addition of sodium sulfate allows the total alkalinity in the cathodic compartment remain constant. However, this strategy presents as a drawback frequent replacements of the anolyte.
- The adoption of a working temperature of  $30^\circ\text{C}$  represents a compromise between the oxygen solubility and the improvement of the kinetic conditions, and the use of sodium silicate as addition agent in the cathodic compartment slightly enhances the current efficiency for alkaline peroxide production.
- An acid anolyte requires a greater chemical resistance for the materials in the anodic compartment and more expensive anodes than those used with alkaline anolyte. Likewise, the cell voltage is enlarged thus increasing the specific energy consumption.

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