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Electrochemical reduction of 2-ethyl-9,10-anthraquinone (EAQ) and mediated formation of hydrogen peroxide in a two-phase medium

Part II: Production of alkaline hydrogen peroxide by the intermediate electroreduction of EAQ in a flow-by porous electrode in two-phase liquid–liquid flow

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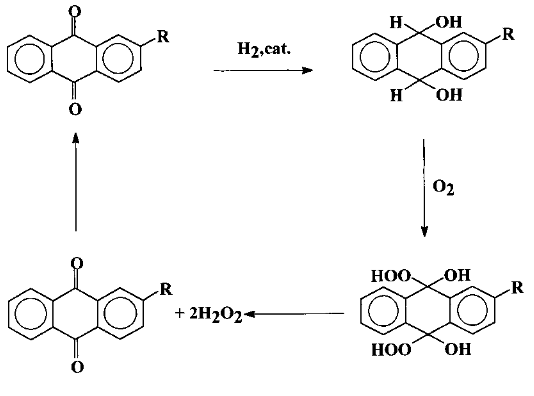
Hydrogen peroxide production by the intermediate electroreduction of the 2-ethyl–9,10-anthraquinone (EAQ) was carried out in a flow-by cell and a two-phase electrolyte formed by a mixture of tributylphosphate (TBP) and diethylbenzene (DEB) as the organic phase, and a solution of NaOH as the aqueous phase. The cathode used was a reticulated vitreous carbon (RVC) foam. We have examined the following process variables: electrolysis current (0.3–3.1 A), catholyte flow rate (470–1630 ml min^{-1}), EAQ concentration in the organic phase (0.21–0.42 M), organic/aqueous phase volume ratio (1/9–4/6) and grade of porosity of the RVC (20–45 ppi). The electrolyses can be carried out in the presence or absence of oxygen gas. The first method is the so-called 'one-step electrolysis' and the second method is the 'two-step electrolysis'. In the second method, the disodium salt of the hydroquinone (EAQNa$_2$) is electrochemically formed in the absence of oxygen. The second step consists of the chemical reaction of this salt with oxygen to form hydrogen peroxide. We obtained a hydrogen peroxide concentration of 0.8 M after 10 A h with an electrolysis current of 1.55 A and a current efficiency of 70%.

Keywords: *2-ethyl-9,10-anthraquinone, oxygen, electroreduction, two-phase, hydrogen peroxide, mediated*

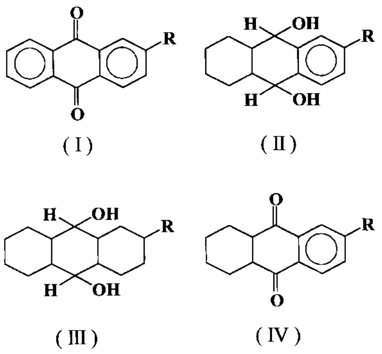
1. Introduction

The industrial process for the preparation of hydrogen peroxide is based on a system using reduction–oxidation cycles of various organic systems. The most important process was developed in Germany during World War II and is based on the catalytic reduction of a 2-alkylanthraquinone. This is the so-called 'anthraquinone process' or the 'AO process'. It represents approximately 85% of the world's production of H_2O_2 [1]. The first step of the 'AO process' consists of the catalytic reduction of the anthraquinone. The 'working solution' containing the anthrahydroquinone is then separated from the hydrogenation catalyst. After the separation, the working solution is aerated with oxygen or air. This oxidation step leads to the quantitative formation of H_2O_2 and regenerates the anthraquinone [2, 3]. This can be summarized by the cyclic Scheme 1.



Scheme 1

During this process, the anthraquinone (I) can form undesired products after the hydrogenation step or the oxidation step. The main degradation product which is formed is the 2-alkyl-5,6,7,8-tetrahydro-9,10-dihydroxyanthracene (II). This byproduct can also lead to the 1,2,3,4,5,6,7,8-octahydroanthrahydroquinone where the substituted ring is hydrogenated (III). The byproduct (II) forms the 2-alkyl-5,6,7,8-tetrahydroanthraquinone (known as 'tetra') (IV) during the oxidation step (Scheme 2).



Scheme 2

Two methods have been developed for carrying out the 'AO process'. The first method, called the 'anthra system', uses conditions which avoid the formation of the tetra by using adapted conditions, i.e. selective catalyst, special solvents etc. The second method, 'all-tetra system', uses the tetra compound. This latter can be hydrogenated and the tetra-hydroquinone obtained can be oxidised with the quantitative formation of H_2O_2. In this case, the quantity of tetra compound increases during the cyclic process. By these two means, it is not possible to completely avoid the formation of other by-products and the global efficiency of the AO process decreases.

The principal electrochemical method to produce hydrogen peroxide is the direct reduction of oxygen. Many tests have been carried out using different experimental conditions; that is, cathode materials, oxygen pressure, electrolyte etc. The formation of hydrogen peroxide by direct reduction of oxygen can be summarized by the following equation:

$$O_2 + 2\,H_2O + 2\,e^- \rightarrow H_2O_2 + 2\,OH^- \quad (1)$$

Globally, the best results for the formation of H_2O_2 by this method were obtained on carbon cathodes. The oxygen reduction on vitreous carbon has been studied in acidic media by Taylor and Humffray [4]. The corresponding reaction is

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \quad (2)$$

In alkaline media, many studies were carried out on different carbon materials [4–8] and the mechanism is better understood. The simplified reaction is

$$O_2 + H_2O + 2\,e^- \rightarrow HO_2^- + OH^- \quad (3)$$

Hydrogen peroxide production by this reaction was examined in a trickle bed reactor by Oloman and Watkinson [9, 10]. The processes developed are not competitive with the AO process except the Dow Process developed in association with Huron Technologies Inc., which offers on-site alkaline peroxide production [11, 12].

Some authors have tried to improve the AO process hydrogenation step which leads to undesired products and requires the filtration of the catalysts. Thus, Lynn and Paalmann have developed a process based on the chemical reduction of the anthraquinone on a sodium amalgam [13, 14].

Other authors have tried to replace the chemical hydrogenation by an electrochemical reduction. Calabrese and Wrighton have tested a photoelectrochemical approach based on the reduction of the 2-*t*-butyl-9,10-anthraquinone in an organic solvent [15]. Keita and Nadjo have tried the electrochemical and photoelectrochemical reduction of 9,10-anthraquinone-2,6-disulfonic acid as an intermediate way of producing hydrogen peroxide [16]. More recently, Knarr *et al.* studied the electrochemical reduction of the 2-ethyl-9,10-anthraquinone (EAQ) in a two-phase system [17]. They produced the disodium salt of the hydroquinone ($EAQNa_2$) in the absence of oxygen in a flow-through cell.

Based on this previous work, we have developed a new electrochemical method to produce alkaline hydrogen peroxide. The method consists of the electrochemical reduction of 2-ethylanthraquinone (EAQ) instead of its catalytic chemical hydrogenation as in the AO process [18]. Thus, the elimination of the catalyst before the oxidation step can be avoided. We have carried out electrolyses in a flow-by electrode cell where the anodic and cathodic compartments were separated by a Nafion® membrane. We have examined the effect of different process variables on hydrogen peroxide production such as: electrolysis current, catholyte flow rate, EAQ concentration in the organic phase, organic/aqueous phase volume ratio and grade of porosity of the RVC.

2. Experimental details

2.1. *Products*

2-ethyl-9,10-anthraquinone (EAQ), tributylphosphate (TBP) and diethyl benzene (DEB) came from Aldrich and were used without further purification. The 2 M NaOH aqueous solution was prepared with sodium hydroxide (Fluka). Concentrated sulfuric acid, sodium thiosulfate, potassium iodide and sodium hypochlorite came from Fluka. All the solutions were prepared with distilled water.

2.2. *Apparatus*

Figure 1 gives an exploded view of the cell. The electrolyte channels are made of Teflon® (c, g and h). The two compartments are separated by a Nafion® 117 cation permeable membrane (e) from DuPont de Nemours. The anode consists of a DSA sheet in contact with several grids of DSA placed in the anolyte stream (b and d). The cathode is a reticulated vitreous carbon (RVC) foam (f), from Energy Research and Generation, Inc.; it is in contact with a 'papiex' sheet supplied by Le Carbone Lorraine (i). On each side of the cell, two stainless steel plates act as electrical connections (a and j). All the elements in contact with the electrolyte flows are separated by gaskets cut from sheets of Viton® (DuPont de Nemours). Figure 2 gives a scheme of the hydraulic circuit.

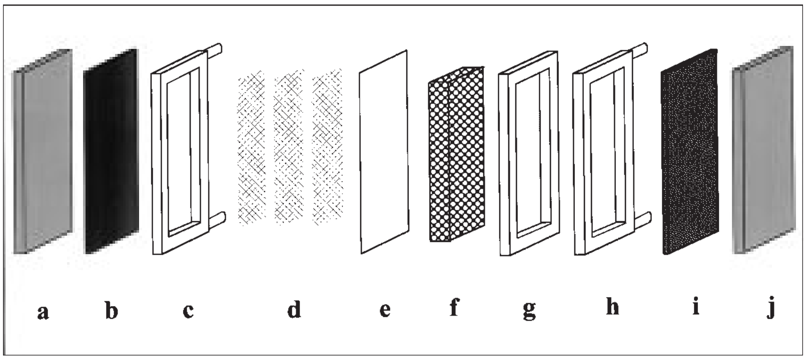


Fig. 1. Details of the electrolysis cell: (a) and (j) stainless steel; (b) and (d) DSA; (c), (g) and (h) Teflon blocks; (e) Nafion® 117 membrane; (f) RVC foam; (I) papiex sheet.

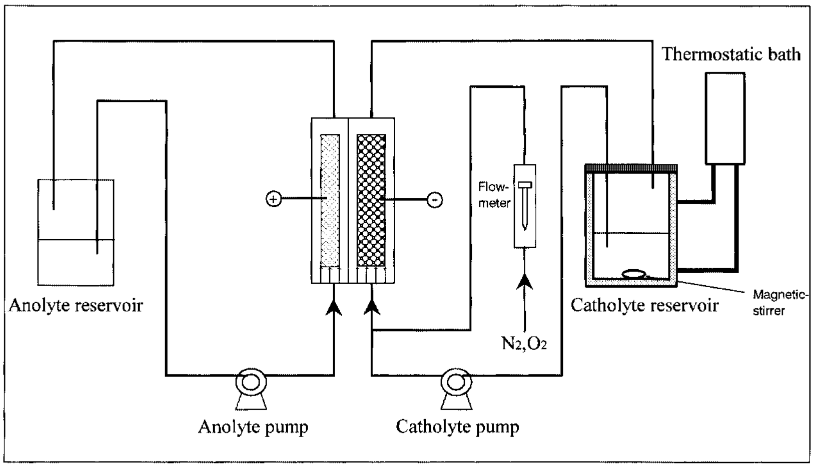


Fig. 2. Scheme of the electrolyte and gas flow circuits.

2.3. *Procedure*

All the electrolyses were done at controlled current, room temperature and atmospheric pressure, for 7 h. The temperature of the catholyte was kept constant by a thermostatic bath. The anolyte remained at room temperature within a few degrees. For all the electrolyses, the cell voltage varied between 2 and 4 V dependent on the current. During the one-step electrolysis, the catholyte was continuously replenished with oxygen which was introduced at the bottom of the cell at a controlled flow rate of 50 ml min^{-1}. The catholyte and the gas flowed concurrently. The introduction of the gas ensured continuous oxygen replenishment of the two-phase catholyte and acted as a turbulence promoter. This action was beneficial as we worked with a two-phase catholyte in a porous electrode. The hydrogen peroxide concentration was monitored as indicated below during the electrolysis. The anolyte, 500 ml of a 2 M NaOH solution, was also continuously recycled at a flow rate of 1200 ml min^{-1} for all the experiments.

The two-step electrolyses were carried out as previously described for the anolyte. The catholyte was first deaerated by bubbling nitrogen for 1 h before starting the electrolysis. During the course of each experiment, a continuous flow of nitrogen was introduced at the bottom of the cell at a flow rate of 50 ml min^{-1}. The disodium salt of hydroquinone concentration was monitored during the electrolysis as described below. At the end of the electrolysis, the second step consisted of replacing the nitrogen flow by an oxygen flow to convert the $EAQNa_2$ into EAQ and to form the alkaline hydrogen peroxide. The end of the chemical conversion of $EAQNa_2$ into EAQ was marked by the disappearance of the burgundy colour of the disodium salt. The efficiency of this conversion was obtained by the determination of hydrogen peroxide concentration.

2.4. *Analytical methods*

The hydrogen peroxide concentration was monitored by a spectrophotometric determination of a Ti(IV)–H_2O_2 complex [19]. A sample of the alkaline aqueous phase was appropriately diluted in a 0.5 M sulphuric acid solution and an addition of a Ti(IV) solution gave a yellow complex.

The disodium salt concentration was monitored by titration. A small sample of the aqueous phase containing the salt was added under nitrogen to a precise quantity of 0.12 M NaOCl solution previously deaerated. The excess of NaOCl was reacted with excess 0.5 M KI solution and the I_2 formed was titrated with

0.1 M thiosulphate. These successive redox reactions gave the $EAQNa_2$ concentration in the aqueous phase.

3. Results and discussion

3.1. *Hydrogen peroxide formation: one-step electrolysis*

The one-step electrolyses were carried out with two organic/aqueous phase volume ratios: 1/9 and 4/6. These phase ratios ensured that the aqueous phase was continuous. The experiments were based on previous work by Knarr *et al.* who studied the maximum ratio of organic to aqueous phase which can be used [17]. They established that with a phase ratio larger than 4/6, the mixture becomes metastable and the organic phase becomes the continuous phase.

3.1.1. Optimization of the experimental parameters. The experiments were carried out with a two-phase catholyte composed of 30 ml of TBP/DEB (15/85, vol/vol) containing the EAQ and 250 ml of 2 M NaOH (phase ratio 1/9). The electrolytes were continuously recycled through the cell.

(a) *Influence of the gas introduction in the cell.* To examine the effect of the introduction of the gas to the cell, we carried out three electrolyses in the two-phase medium describe above. The organic phase contained 100 g dm^{-3} of EAQ (0.42 M). The RVC grade of porosity was 20 ppi ($a_e = 10\,cm^{-1}$) and the dimensions of the cathode were 5.7 cm × 10.7 cm × 2.5 cm leading to a total area of 1525 cm^2. The electrolysis current was 0.3 A (5 mA cm^{-2} for projected area). The catholyte flow rate was 474 ml min^{-1}. The first electrolysis was carried out with no gas in the cell and the $EAQNa_2$ which was formed in the cathodic compartment was completely oxidized at the outlet of the cell by sparging through the catholyte a stream of oxygen (50 ml min^{-1}). Thus no $EAQNa_2$ was recycled in the cell. The second electrolysis was carried out under the same conditions with an introduction of nitrogen gas flow of 50 ml min^{-1} at the bottom of the cell. The $EAQNa_2$ was oxidized at the outlet of the cell. The third electrolysis was carried out with introduction of an oxygen flow of 50 ml min^{-1} at the bottom of the cell. Figure 3 gives the results obtained. We observed that, in the presence of nitrogen gas in the cell (Fig. 3, curves (b)), the mass transfer for the reduction of EAQ is improved. The gas bubbles act as a turbulence promoter. In the absence of oxygen in the cell, the $EAQNa_2$ is formed by the following reaction:

$$EAQ_{(org)} + 2\,e^- + 2\,Na^+ \rightarrow EAQNa_{2\,(aq)} \qquad (4)$$

In the presence of oxygen, the following chemical reaction produces hydrogen peroxide:

$$EAQNa_2 + O_2 + H_2O \rightarrow EAQ + HO_2^- + OH^- + 2\,Na^+ \qquad (5)$$

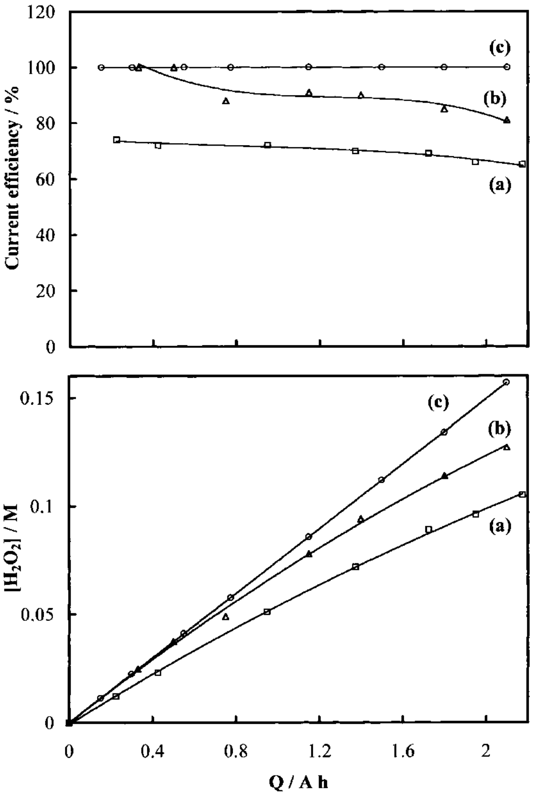


Fig. 3. Comparison of hydrogen peroxide formation in TBP/DEB (15/85, vol/vol) + EAQ (100 g dm^{-3}) + 2 M NaOH (90 vol %); RVC 20 ppi ($a_e = 10\,cm^{-1}$, 2.5 cm × 5.7 cm × 10.7 cm, $a_T = 1525\,cm^2$); electrolysis current 0.3 A (5 mA cm^{-2} for projected area); catholyte flow rate 470 ml min^{-1}: (a) without gas in the cell, (b) with nitrogen flow in the cell (50 ml min^{-1}) and (c) with oxygen flow in the cell (50 ml min^{-1}).

In the presence of oxygen gas in the cell, the gas bubbles act, as before, as a turbulence promoter and, more important, the medium is continuously replenished with dissolved oxygen. The salt is immediately consumed in the chemical reaction with oxygen to produce hydrogen peroxide. Thus, the $EAQNa_2$ concentration is held near zero. In the continuously oxygen replenished medium, the hydrogen peroxide is probably mainly formed by the reaction of oxygen with the reduced form of EAQ in the organic phase before the formation of the salt in the aqueous phase [18]. This possibility is expressed by the following equations:

$$EAQ + 2\,e^- \rightarrow EAQ^{2-} \qquad (6)$$

$$EAQ^{2-} + O_2 \rightarrow EAQ + O_2^{2-} \qquad (7)$$

$$O_2^{2-} + H_2O \rightarrow HO_2^- + OH^- \qquad (8)$$

We also can not exclude the direct reduction of O_2 at the electrode surface:

$$O_2 + H_2O + 2\,e^- \rightarrow HO_2^- + OH^- \qquad (3)$$

The current efficiency of 100% shows that the reduction of HO_2^- to OH^- by Reaction 10 is almost avoided in these conditions.

Maintaining the $EAQNa_2$ concentration near zero is an absolute condition to obtain good current efficiencies. This is easily achieved as the formation of the salt is marked by the appearance of an intense burgundy colour; thus we can modify instantaneously the catholyte flow rate, which directly acts on this formation. Indeed, we have observed that for one electrolysis current, there is an optimum combination between the catholyte flow rate and the gas flow rate in order to obtain a maximum hydrogen peroxide production.

The principal reason for avoiding the formation of the disodium salt is its chemical oxido-reduction reaction with hydrogen peroxide. This reaction can be expressed by

$$\begin{aligned} &\mathrm{EAQNa_2 + HO_2^- + H_2O} \\ &\quad \rightarrow \mathrm{EAQ + 3\,OH^- + 2\,Na^+} \end{aligned} \qquad (9)$$

Reaction 9 has been studied in detail in our laboratory. We have observed that the chemical conversion of oxygen into hydrogen peroxide by Reaction 5 gives high efficiencies when the disodium salt concentration is low. In contrast, when the disodium salt concentration is high, the efficiency of the conversion is low [20].

(b) *Influence of the combined effect of the electrolysis current and catholyte flow rate.* In these experiments, we used the same two-phase medium and RVC cathode as before. The catholyte flow rate was adjusted for each electrolysis current at the beginning of the experiment. It was increased until there was no disodium salt leaving the cell. Thus the catholyte flow rate obtained corresponded to a system where the salt was not produced or instantaneously oxidised [18]. Figure 4 shows these results. A current of 1.37 A and a catholyte flow rate of 1300 ml min^{-1} gives the best results.

(c) *Influence of the EAQ concentration.* For these experiments, we used the same two-phase medium and RVC cathode as described before. We compared two concentrations of EAQ in the organic phase: 50 and 100 g dm^{-3}. The electrolysis current was 1.37 A (22.5 mA cm^{-2} based on projected area). The catholyte flow rate was 1300 ml min^{-1}. The oxygen flow rate was 50 ml min^{-1}. Figure 5 shows the results.

The mixture containing 100 g dm^{-3} of EAQ provides the best results, it corresponds to the nearly saturated medium in EAQ at ambient temperature. As the hydrogen peroxide production is mediated by the electroreduction of EAQ, it is clearly evident that the mediator concentration must be as high as possible.

(d) *Comparison of the production of hydrogen peroxide by the intermediate reduction of EAQ to the formation of H_2O_2 by direct reduction of oxygen.* In this comparison, we used the same experimental conditions as before. The electrolyses were carried out in the following media: the first consisted of the two-phase medium made of 30 ml TBP/DEB (15/85, vol/vol) + EAQ (100 g dm^{-3}) + 250 ml 2 M NaOH, the second medium was 30 ml TBP/DEB (15/85, vol/vol) without EAQ + 250 ml 2 M NaOH and the third medium was 250 ml of 2 M NaOH. Figure 6 shows the results.

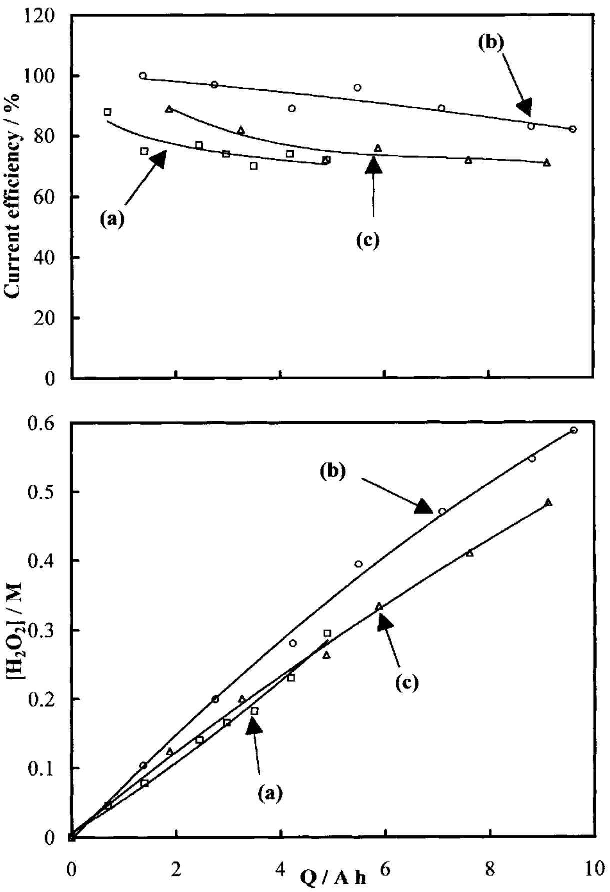


Fig. 4. Influence of the electrolysis current on the hydrogen peroxide formation by intermediate electroreduction of EAQ on a RVC 20 ppi cathode (a_e = 10 cm^{-1}, 2.5 cm × 5.7 cm × 10.7 cm, a_T = 1525 cm^2) in TBP/DEB (15/85, vol/vol) + EAQ (100 g dm^{-3}) + 2 M NaOH (90 vol %); oxygen flow rate 50 ml min^{-1}: (a) electrolysis current 0.7 A (11.5 mA cm^{-2} for projected area), catholyte flow rate 970 ml min^{-1}; (b) electrolysis current 1.37 A (22.5 mA cm^{-2} for projected area), catholyte flow rate 1300 ml min^{-1}; and (c) electrolysis current 1.5 A (24.6 mA cm^{-2} for projected area), catholyte flow rate 1500 ml min^{-1}.

In the one-phase medium (Fig. 6, curves (c)), hydrogen peroxide formed is further reduced. This phenomenon is described by the following equations:

$$\mathrm{O_2 + 2\,e^- + H_2O \rightarrow HO_2^- + OH^-} \qquad (3)$$

$$\mathrm{HO_2^- + 2\,e^- + H_2O \rightarrow 3\,OH^-} \qquad (10)$$

In this medium, we also observed the reduction of water:

$$\mathrm{2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-} \qquad (11)$$

In the two-phase medium without EAQ (Fig. 6, curves (b)), hydrogen peroxide is formed by Reaction 3. The loss by Reaction 10 is not so marked as before. It is likely that the dissolved oxygen in the organic phase is reduced at the electrode/organic phase interface and is then extracted in the aqueous phase where it is partially protected from further reduction. Indeed, the organic phase has more affinity with RVC than the aqueous phase containing the hydrogen peroxide.

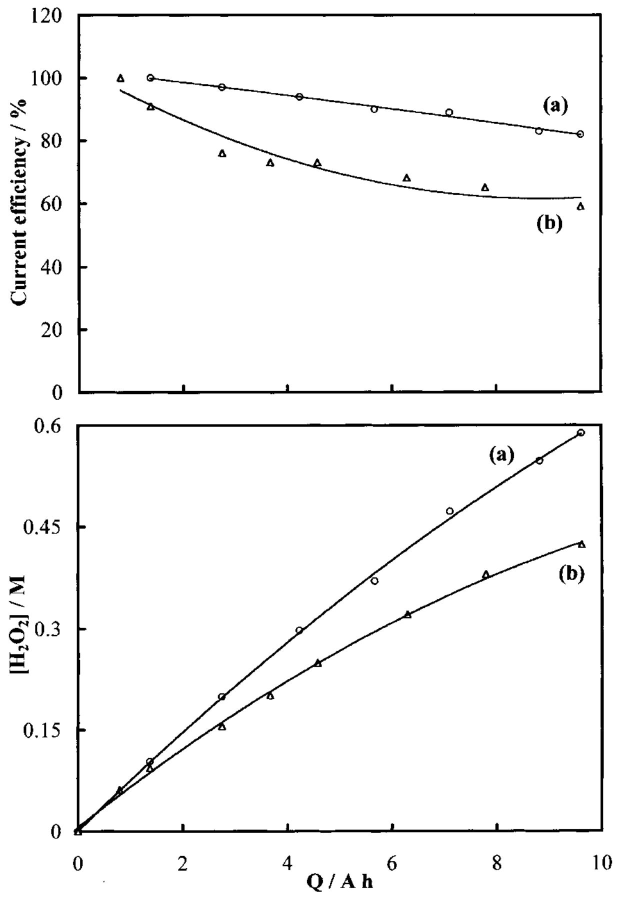


Fig. 5. Comparison of hydrogen peroxide formation in TBP/DEB (15/85, vol/vol) + different EAQ concentrations + 2 M NaOH (90 vol %); RVC 20 ppi (a_e = 10 cm^{-1}, 2.5 cm × 5.7 cm × 10.7 cm, a_T = 1525 cm^2); electrolysis current 1.37 A (22.5 mA cm^{-2} for projected area); catholyte flow rate 1300 ml min^{-1}; oxygen flow rate 50 ml min^{-1}: (a) [EAQ] = 100 g dm^{-3} and (b) [EAQ] = 50 g dm^{-3}.

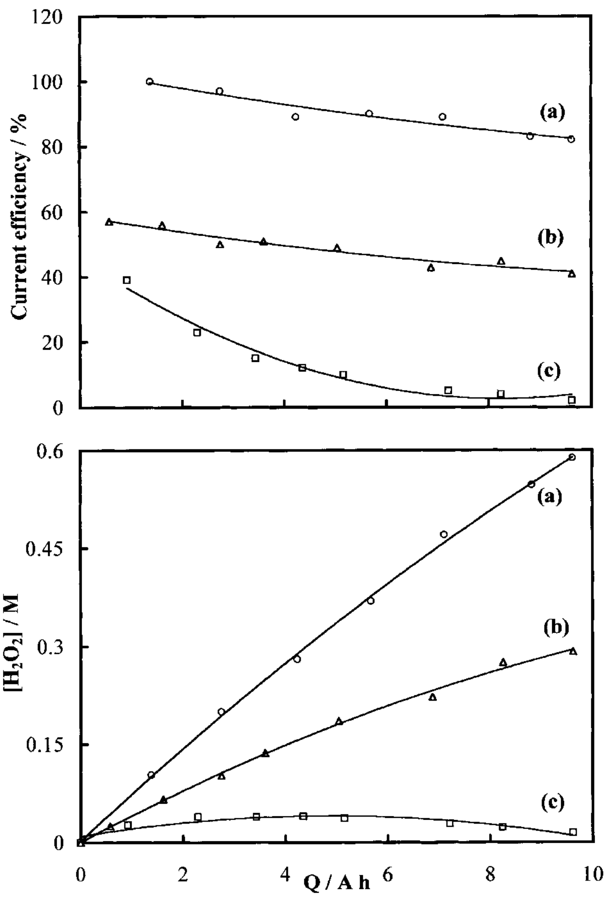


Fig. 6. Comparison of hydrogen peroxide formation by intermediate electroreduction of EAQ with its formation by direct oxygen reduction; RVC 20 ppi (a_e = 10 cm^{-1}, 2.5 cm × 5.7 cm × 10.7 cm, a_T = 1525 cm^2); electrolysis current 1.37 A (22.5 mA cm^{-2} for projected area); catholyte flow rate 1300 ml min^{-1}; oxygen flow rate 50 ml min^{-1}: (a) in 30 ml TBP/DEB (15/85, vol/vol) + EAQ (100 g dm^{-3}) + 250 ml 2 M NaOH; (b) in 30 ml TBP/DEB (15/85, vol/vol) + 250 ml 2 M NaOH; and (c) in 250 ml NaOH 2 M.

In the two-phase medium containing the EAQ (Fig. 6, curves (a)), hydrogen peroxide is mainly formed by chemical reaction between the reduced quinone and the dissolved oxygen. As mentioned above, there are two possibilities to produce hydrogen peroxide. The first is a reaction between the disodium salt, formed in the aqueous phase, and oxygen, this reaction is expressed by Equation 5. The second is a chemical reaction in the organic phase between the dianion (EAQ^{2-}) and oxygen; this corresponds to Equations 6 to 8. The second possibility seems to be the most likely as we have never observed the formation of the salt after the adjustment of the catholyte flow rate at the beginning of the electrolysis.

(e) *Influence of the RVC porosity.* We carried out several electrolyses using a RVC 45 ppi cathode (a_e = 28 cm^{-1}, 2.5 cm × 5.7 cm × 10.7 cm, a_T = 4269 cm^2). We examined the combined effect of the electrolysis current and the catholyte flow rate. Figure 7 shows the best results for each electrolysis current experimented. For each electrolysis current, the results are not as good as for the electrolyses on RVC 20 ppi. When we increase the electrolysis current from 0.82 to 1.37 A, the results are better (Fig. 7, curves (a), (b) and (c)). In this case the electroreduction of EAQ is improved and the oxygen dissolved is sufficient to convert all the reduced form EAQ^{2-} in the EAQ and to produce hydrogen peroxide simultaneously. At an electrolysis current of 1.64 A (Fig. 7, curves (d)), we observed a small production of hydrogen peroxide associated with a consequent decrease in current efficiency. At this current, there is no problem in obtaining a good conversion of the reduced form of EAQ and in avoiding the formation of the disodium salt. It seems that the low results are due to the reduction of hydrogen peroxide in water. In the electrolyses on a RVC 45 ppi cathode, there is a different phenomenon. We observed that the organic phase remains in the porous cathode and the catholyte in circulation is essentially formed by the aqueous phase. The cell voltage is increased and the cathodic potential reaches values at which hydrogen peroxide is reduced.

3.1.2. *Hydrogen peroxide formation with 40% of organic phase.*

The maximum organic/aqueous phase volume ratio to obtain a continuous aqueous conducting phase was determined by Knarr *et al.* to

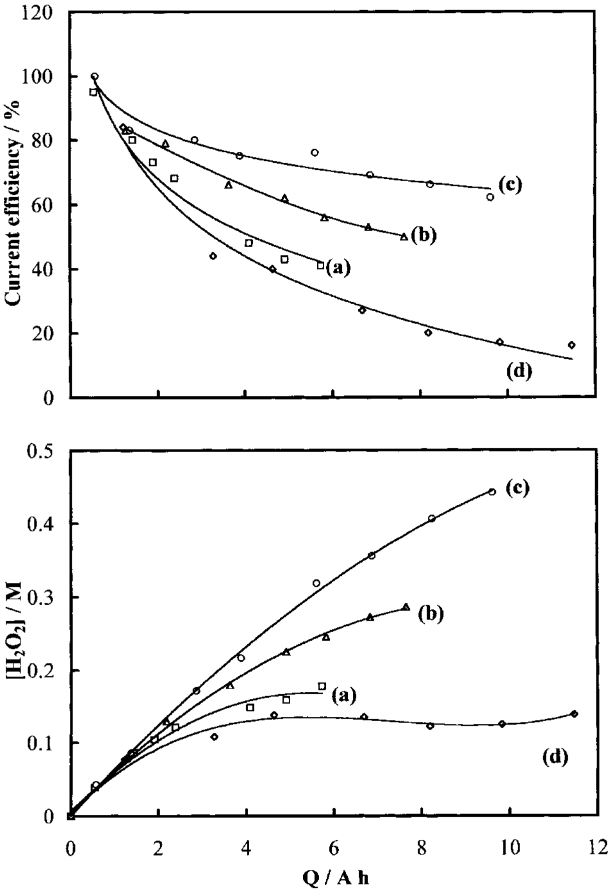


Fig. 7. Influence of the electrolysis current on the hydrogen peroxide formation by intermediate electroreduction of EAQ on a RVC 45 ppi cathode (a_e = 28 cm^{-1}, 2.5 cm × 5.7 cm × 10.7 cm, a_T = 4269 cm^2) in TBP/DEB (15.85, vol/vol) + EAQ (100 g dm^{-3}) + 2 M NaOH (90 vol %); oxygen flow rate 50 ml min^{-1}: (a) electrolysis current 0.82 A (13.4 mA cm^{-2} for projected area), catholyte flow rate 800 ml min^{-1}; (b) electrolysis current 1.09 A (17.9 mA cm^{-2} for projected area), catholyte flow rate 1220 ml min^{-1}; (c) electrolysis current 1.37 A (22.5 mA cm^{-2} for projected area), catholyte flow rate 1300 ml min^{-1}; and (d) electrolysis current 1.64 A (26.9 mA cm^{-2} for projected area), catholyte flow rate 1420 ml min^{-1}.

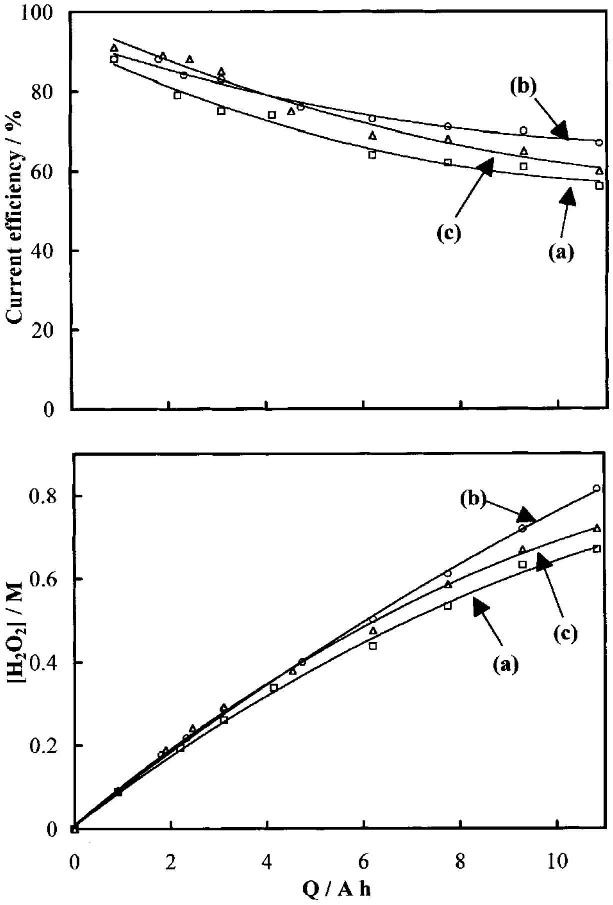


Fig. 8. Influence of the catholyte flow rate on the hydrogen peroxide formation in TBP/DEB (15/85, vol/vol) + EAQ (100 g dm^{-3}) + 2 M NaOH (60 vol %); RVC 20 ppi (a_e = 10 cm^{-1}, 2.5 cm × 5.7 cm × 10.7 cm, a_T = 1525 cm^{-2}); electrolysis current 1.55 A (25.4 mA cm^{-2} for projected area); oxygen flow rate 50 ml min^{-1}; catholyte flow rate: (a) 800, (b) 1300 and (c) 1630 ml min^{-1}.

be 4/6 [17]. Thus, experiments were carried out with the following two-phase catholyte: 168 ml of 2 M NaOH and 112 ml of TBP/DEB (15/85, vol/vol) containing the EAQ (100 g dm^{-3}). The RVC 20 ppi cathode was the same as used in previous electrolyses.

We carried out experiments at two different electrolysis currents with different catholyte flow rates. The first current was 1.55 A (25.4 mA cm^{-2} projected area). Figure 8 shows the results with three catholyte flow rates. The first catholyte flow rate was 800 ml min^{-1} (Fig. 8, curves (a)). This corresponds to a system of which continuous replenishment of oxygen is insufficient to consume all the disodium salt formed in the cell. In this case we observed that some salt leaves the cell and is oxidised outside the cell before it is recycled. This phenomenon can easily be observed due to the characteristic colour of the disodium salt of the hydroquinone. The stationary concentration of this salt is not minimized and it can be oxidised by hydrogen peroxide to produce the quinone and to induce a loss in hydrogen peroxide. This is explained by Reaction 9, which is responsible for the decrease in current efficiencies. The second catholyte flow rate was 1300 ml min^{-1} (Fig. 8, curves (b)), and corresponds to the optimum in which no salt exits the cell. In this case, we have reduced the stationary concentration of the salt and the probability of reaction with hydrogen peroxide is near zero. The third catholyte flow rate, 1630 ml min^{-1}, induces a modification of the mass transport conditions which become less efficient.

We carried out the same experiments with an electrolysis current of 3.1 A (50.8 mA cm^{-2} projected area). Figure 9 shows the results for three catholyte flow rates. The same phenomena as previously are observed.

As for 10% organic phase, we compared hydrogen peroxide production by the mediated electroreduction of EAQ with the direct reduction of oxygen under the same conditions. For these experiments, we used the same RVC cathode as previously. The electrolysis current was 1.55 A (25.4 mA cm^{-2} projected area) and the catholyte flow rate was 1300 ml min^{-1}. The oxygen flow rate was 50 ml min^{-1}. The electrolyses were carried out in the following media: the first consisted of 112 ml TBP/DEB

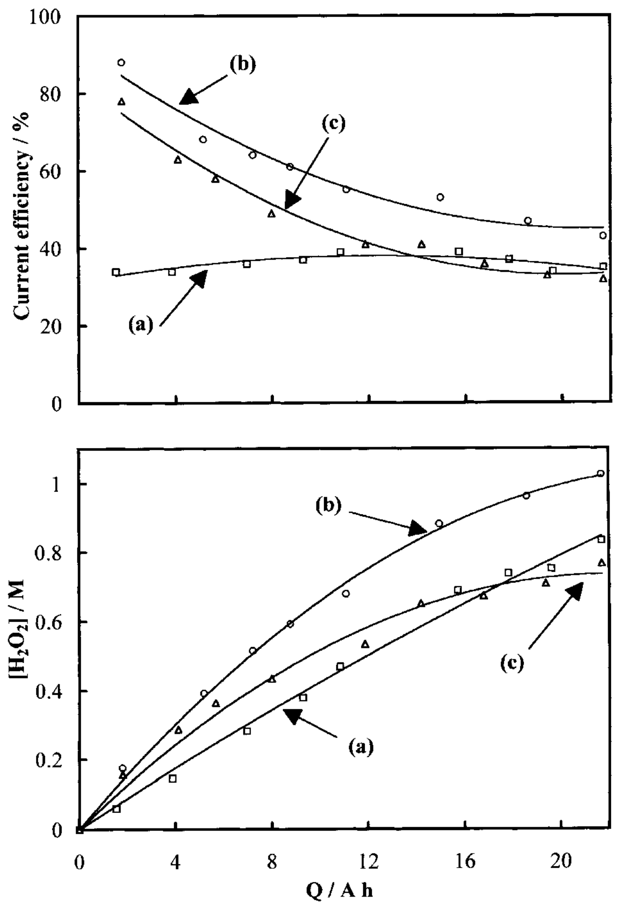


Fig. 9. Influence of the catholyte flow rate on the hydrogen peroxide formation in TBP/DEB (15/85, vol/vol) + EAQ (100 g dm^{-3}) + 2 M NaOH (60 vol%); RVC 20 ppi (a_e = 10 cm^{-1}, 2.5 cm × 5.7 cm × 10.7 cm, a_T = 1525 cm^2); electrolysis current 3.1 A (50.8 mA cm^{-2} for projected area); oxygen flow rate 50 ml min^{-1}; catholyte flow rate: (a) 1100, (b) 1400 and (c) 1630 ml min^{-1}.

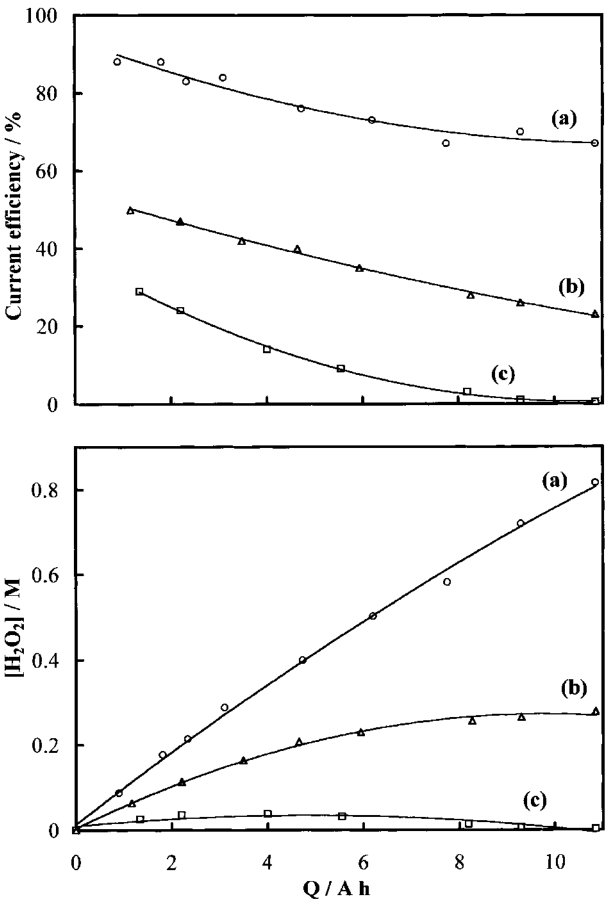


Fig. 10. Comparison of hydrogen peroxide formation by intermediate electroreduction of EAQ with its formation by direct oxygen reduction; RVC 20 ppi (a_e = 10 cm^{-1}, 2.5 cm × 5.7 cm × 10.7 cm, a_T = 1525 cm^2); electrolysis current 1.55 A (25.4 mA cm^{-2} for projected area); catholyte flow rate 1300 ml min^{-1}; oxygen flow rate 50 ml min^{-1}: (a) in 112 ml TBP/DEB (15/85, vol/vol) + EAQ (100 g dm^{-3}) + 168 ml 2 M NaOH; (b) in 112 ml TBP/DEB (15/85, vol/vol) + 168 ml 2 M NaOH; and (c) in 168 ml NaOH 2 M.

(15/85, vol/vol) + EAQ (100 g dm^{-3}) + 168 ml 2 M NaOH, the second was 112 ml TBP/DEB (15/85, vol/vol) without EAQ + 168 ml 2 M NaOH and the third was 168 ml of 2 M NaOH. Figure 10 shows these results. The best results were observed with the two-phase medium containing the quinone (Fig. 10, curves (a)). In the cases without EAQ, the reasons for the decrease in current efficiencies are the same as described in paragraph 3.1.1(d).

3.2. *Hydrogen peroxide formation: two-step electrolysis*

All the experiments were carried out with a two-phase catholyte composed of 168 ml of 2 M NaOH and 112 ml of TBP/DEB (15/85, vol/vol) containing the EAQ (100 g dm^{-3}). The catholyte was deaerated and continuously recycled through the cell. The cathode was the same 20 ppi RVC as before.

Various currents and catholyte flow rates were used. The theoretical charge to obtain total conversion of the EAQ in the organic phase to EAQNa$_2$ was calculated from Faraday's law as a function of the EAQ quantity. For our case this was 2.54 A h. The corresponding duration for each electrolysis was also calculated as a function of current. Thus, for a current of 1.55 A (25.4 mA cm^{-2} projected area), 3.1 A (50.8 mA cm^{-2} projected area) and 6.2 A (101.7 mA cm^{-2} projected area), the following electrolysis durations: 98, 49 and 25 min, respectively, were obtained.

Tables 1 to 3 summarize these results. R_e refers to the current efficiency for the electrochemical conversion of the EAQ to EAQNa$_2$ at the end of the electrolysis; R_c refers to the efficiency for the chemical formation of alkaline H_2O_2 in the oxidation reaction of EAQNa$_2$ to EAQ by O_2.

It can be seen that for each current, the catholyte flow rate is an important variable and must be adjusted to get the best conditions for the mass transfer

Table 1. Results for the electrolysis carried out at 1.55 A for 98 min

Catholyte flow rate /ml min^{-1}	*[EAQNa$_2$]* /M	*R_e* /%	*[H_2O_2]* /M	*R_c* /%
1100	0.222	77	0.153	69
1300	0.204	70	0.134	65
1630	0.188	65	–	–

Table 2. Results for the electrolysis carried out at 3.1 A for 49 min

Catholyte flow rate /ml min^{-1}	*[EAQNa$_2$]* /M	*R$_e$* /%	*[H$_2$O$_2$]* /M	*R$_c$* /%
1100	0.225	78	0.130	58
1300	0.223	78	0.124	49
1630	0.221	77	0.136	62

Table 3. Results for the electrolysis carried out at 6.2 A for 25 min

Catholyte flow rate /ml min^{-1}	*[EAQNa$_2$]* /M	*R$_e$* /%	*[H$_2$O$_2$]* /M	*R$_c$* /%
1100	0.127	45	0.106	84
1300	0.149	52	0.104	70
1630	0.127	45	0.086	68

of the EAQ to the electrode surface. For the formation of hydrogen peroxide by the conversion of the disodium salt into EAQ, the best result was observed for the lowest disodium salt concentration. The low efficiency for the formation of hydrogen peroxide during the chemical oxidation of EAQNa$_2$ to EAQ by O$_2$ are due to chemical reaction between EAQNa$_2$ and the hydrogen peroxide as described above, see Equation 9.

Under the same electrolysis conditions, when the hydrogen peroxide production by the one-step electrolysis is compared with the disodium salt production by the two-step electrolysis, the salt production is always lower than the hydrogen peroxide formation.

In conclusion, these experiments show that the disodium salt concentration must be kept near zero, as described for the one-step electrolysis, in order to get the best efficiency for hydrogen peroxide production.

4. Conclusion

We have developed a new electrochemical method to produce alkaline hydrogen peroxide. It consists of the intermediate electroreduction of EAQ in a two-phase medium on a RVC cathode in the presence of oxygen. The EAQ is dissolved in an organic phase formed by a mixture of TBP and DEB (15/85, vol/vol). The second phase is a 2 M NaOH solution. The process, which works at room temperature and pressure, involves continuous recycle of the electrolytes. The electrolyses were carried out in a flow-by cell. The cell voltages varied between 2 and 4 V depending on the electrolysis current. The effect of the current, catholyte flow rate, EAQ concentration in the organic phase, organic/aqueous phase volume ratio and grade of RVC porosity were examined. We have established that the organic phase must be as concentrated as possible in EAQ; the proportion of this phase must be as high as possible but the aqueous phase must remain the continuous phase. The catholyte flow rate must be adjusted for each electrolysis current.

Comparison of the best results obtained after 10 A h with 10% and 40% of organic phase (Fig. 4(b) and 8(b)) gives: current efficiency 85% and 70%, concentration of hydrogen peroxide in the aqueous phase 0.6 M and 0.8 M, respectively, with approximately the same current (1.37 A and 1.55 A) and the same catholyte flow rate (1300 ml min^{-1}). These results show that, from the point of view of current efficiency for hydrogen peroxide production, a low organic/aqueous phase volume ratio is favourable; from the point of view of hydrogen peroxide concentration, a high ratio is favourable. As shown in Fig. 9(b), a high organic/aqueous phase volume ratio allows the use of 3.1 A with only a small decrease in current efficiency (60% after 10 A h) and of the hydrogen peroxide concentration (0.65 M after 10 A h). Of course, the time necessary to reach 10 A h must be divided by two in this case.

Finally, in terms of current efficiency, hydrogen peroxide production by one-step electrolysis is always more efficient than by two-step electrolysis.

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