A Convergent Electrosynthesis for Chlorine Dioxide

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A promising approach in green electrochemistry involves the minimization of energy expenditure through the design of systems performing useful reactions at both electrodes of an electrosynthetic cell (i.e., simultaneous processes). A proof-of-concept for the rather unusual simultaneous production of one substance (i.e., ClO_2) at both electrodes was reported earlier by us, and we provide further insight in the present study. This *convergent* process involves the (indirect) reduction of ClO_3^- at the cathode, and the direct oxidation of ClO_2^- at the anode of a divided cell. High acidity is required in the catholyte, whereas neutral conditions suffice at the anolyte. Such a large pH gradient between both compartments necessitates an intermediate compartment to prevent electrolyte interaction, as the passage of H_3O^+ from the former to the latter would chemically produce ClO_2 and thus interfere with the monitoring of its solely electrochemical production. A system was designed that effectively prevents proton migration by using two anionic exchange membranes, AEM combined with a fine pore fritted glass (AEM/fritted glass/AEM). A spectroelectrochemical technique was developed to monitor the production of ClO_2 in situ and in real time at its characteristic absorption wavelength (359 nm) by adapting a normal rectangular spectrophotometer quartz cell to serve as electrolytic cell inside a spectrophotometer. The corresponding yields were highly dependent on the applied potential: the cathodic production was favored at an applied potential near the rest potential, whereas the anodic production behaved in an inverse manner. Exploratory experiments produced an overall yield of ca. 10% after a reaction time of 30 min.

Keywords: chlorine dioxide; chlorite oxidation; chlorate reduction; convergent paired process; electrosynthesis; ClO_2

1. INTRODUCTION

A promising *green electrochemistry* approach in electrosynthetic cells involves the design of systems that generate useful reactions at both electrodes (i.e., simultaneous and paired processes).[1-6] In addition to the economic and energy savings, benefits of designing and using simultaneous processes also include a reduced consumption of fossil fuels in producing electricity, and the attendant decrease in pollution. The production of useful substances instead of worthless byproducts also avoids the need for their separation and the concomitant waste disposal.[6] Simultaneous electrosynthesis can yield one or two main substances as shown below.

a) Production of a single main substance. Examples include:
i. conversion of propylene to propylene oxide[4]
ii. production of $NaBrO_3$[7]
iii. dehydration of HNO_3 to form N_2O_5 [2]
iv. production of chloroacetic acid[8]

b) Production of two substances of interest
i. Here, the same starting material is oxidized at one electrode and reduced at the other. For example, the electrolysis of glucose yields gluconic acid at the anode and sorbitol at the cathode.[2]
ii. The product of the anodic reaction becomes the main reactant for the cathodic reaction. A good example involves the sequence: 2,3 butanediol $\rightarrow$ acetoine $\rightarrow$ 2-butanone.[9]
iii. The products from both electrodic reactions are useful substances. Examples include the chlor-alkali process, the production of Pb chromate (and/or dichromate) in the anolyte and NaOH in the catholyte,[10] and the co-production of ClO_2 and NaOH from a solution of $NaClO_3$ and HCl.[11]

c) Convergent paired synthesis. There are also cases where both electrodic reactions produce simultaneously the same product (unfortunately these are rather infrequent cases). Examples include:
i. production of anthraquinone[12]
ii. production of 1,4 naphtoquinone[13]
iii. production of Cu_2O[2]

Other simultaneous electrosynthetic processes have been reviewed elsewhere[1,2,4] and we have summarized several proposed applications for the environmental electrochemistry arena.[5,6,14] In particular, we have been interested in achieving the convergent electrosynthesis of ClO_2 (an effective disinfecting and bleaching agent)[16-19] and reported its first proof-of-concept.[6,15] We have investigated selected mechanistic aspects of the production of ClO_2 by the indirect cathodic reduction of ClO_3^- using voltammetric and spectroelectrochemical techniques.[20] To better understand the convergent process, the reduction reaction is coupled to the anodic production of ClO_2 through oxidation of ClO_2^- and both are studied quantitatively in situ and in real time.

2. EXPERIMENTAL

Solutions were prepared from $NaClO_3$ (Sigma, 99.8%), $NaClO_2$ (Aldrich, 80%), H_2SO_4 (J. T. Baker, 98%), and Na_2SO_4 (J. T. Baker, ACS, 100.3%). Linear sweep voltammograms were obtained in a conventional three-electrode system with a CV-50W potentiostat (Bioanalytical Systems, BAS). The aqueous samples (2.0 mL) were contained in 3-mL conical-bottom vials masked with black electrical tape to prevent photochemical product decomposition[20] and equipped with Teflon caps having the necessary perforations to allow for electrode and purging gas line insertion. The working electrode in each cell was a Pt disk (BAS, MF 2013, $\Phi = 1.6$ mm). The counter electrode was a graphite rod (Steadtler Mars HB, diameter = 2 mm, length = 7 cm, immersed portion = 5 cm). The reference electrode was Ag/AgCl (BAS, MF 2052) and all the potentials here are referred to it. To prevent cross contamination, this electrode was separated from the electrolytic medium by placing it inside a special glass compartment (BAS, MF-2064) containing 0.1 M Na_2SO_4 that made electrical contact with the working solution through a fine vycor frit. Ionic exchange membranes were tested as separators, including a cation exchange membrane, CEM (Nafion 417, Aldrich) and an anion exchange membrane, AEM (The Electrosynthesis Co., R-1030). A fine-pore fritted glass disk ($\Phi = 1.5$ cm) served as a physical separator as described below.[19]

The production of ClO_2 was monitored in situ and in real time at its characteristic absorption wavelength (359 nm) during the spectroelectrochemical experiments by adapting a normal rectangular spectrophotometer quartz cell (1-cm path length, 4-mL capacity) to serve as the electrolytic cell inside a UV-VIS Cary 300 Varian spectrophotometer. Typical runs comprised 10 cycles (1 cycle = 900 nm)/min), except for fixed-wavelength scans. To permit the passage of light, a Pt mesh (Aldrich, 100 mesh, 99.9% pure) was used as working electrode. The entire cell arrangement was kept inside the spectrophotometer for the duration of each test (i.e., 10 min unless otherwise noted). A twin quartz cell containing a similar Pt mesh was placed in the reference compartment of the spectrophotometer for signal correction. The ex-situ absorbances were measured in a Perkin Elmer spectrophotometer (model Spec 20). Current responses were tracked at various constant potentials. A more detailed description of the experimental system can be found elsewhere.[19,20]

Deionized water was used in all the solutions. Each test solution was deaerated by passing high purity nitrogen (Infra) for 5 min prior to an electrochemical experiment, and a nitrogen blanket was maintained above the solution for the duration of each test. The highly acidic nature required in the catholyte and the neutral conditions at the anolyte in the simultaneous experiments necessitated an intermediate compartment to prevent their interaction, since passage of H_3O^+ from the former to the latter would chemically produce ClO_2 and thus interfere with the monitoring of its solely electrochemical production. For this purpose, an intermediate compartment was inserted to separate these two electrolytic chambers (each one contained in a 10-mL conical-bottom vial). See Figures 1 and 2.[19] Cationic and anionic exchange membranes, as well as a fine pore glass frit, were tested in search of an effective electrolyte separation as described below.
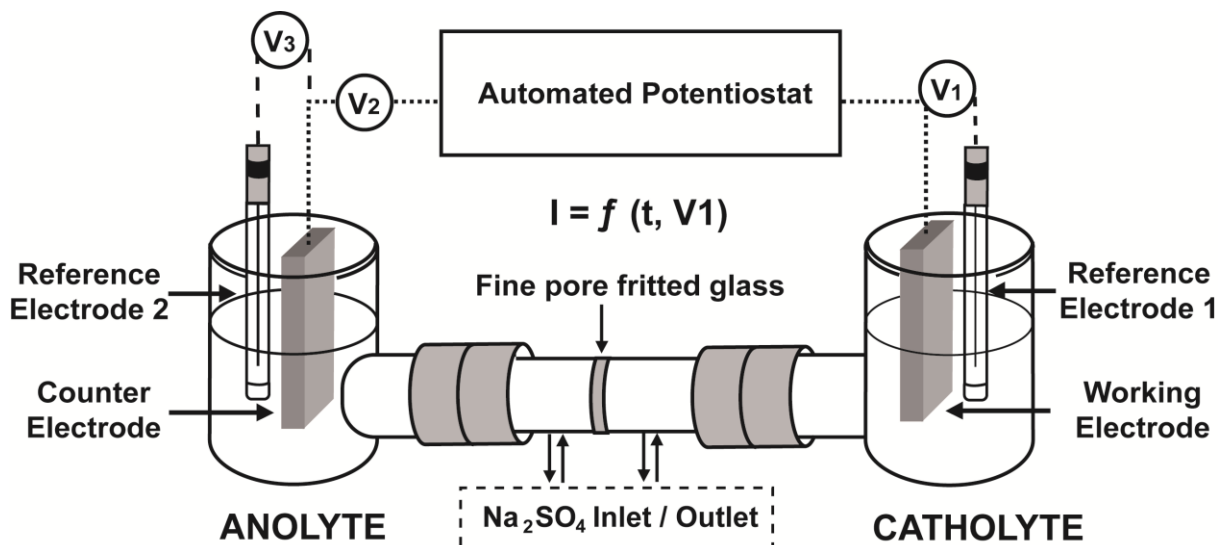
Figure 1. Experimental setup for the convergent electrosynthesis.
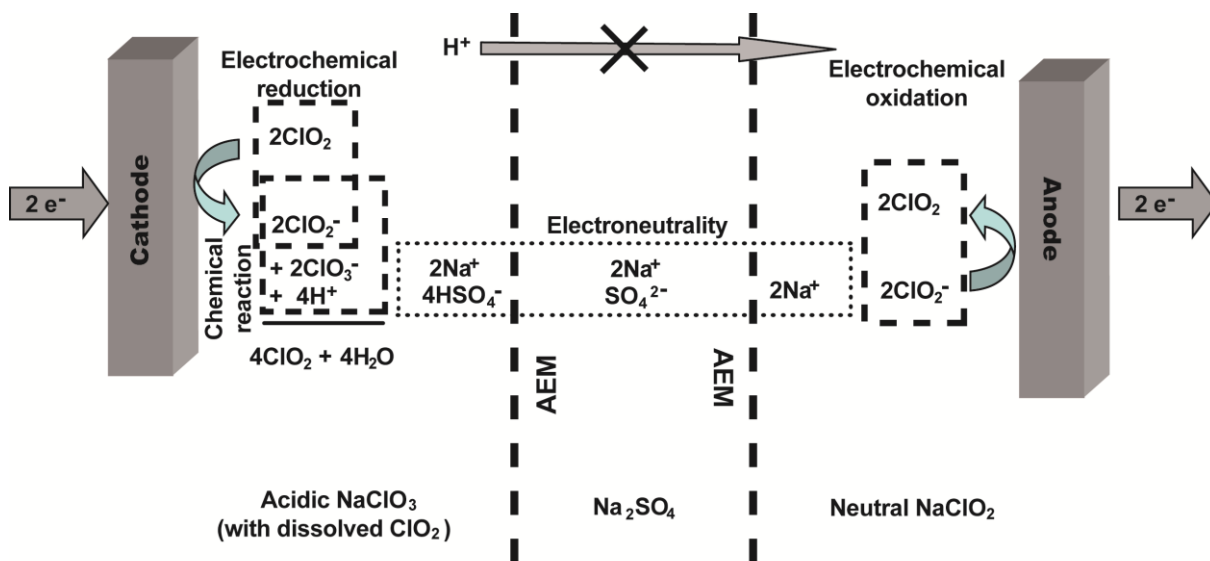

Figure 2. Experimental model.

3. RESULTS AND DISCUSSION

3.1 Electrochemical oxidation of $NaClO_2$

In order to map the anodic response of 0.01 M $NaClO_2$ linear sweep voltammograms, LSV were run from the rest potential (at ca. 600 mV vs. Ag/AgCl) up to that where massive solvent decomposition occurred (ca. 1800 mV). An oxidation signal peaked at ca. 950 mV (Figure 3). For comparison, $NaClO_3$ and ClO_2 scans were also run. These do not show evidence of oxidation in this potential range.
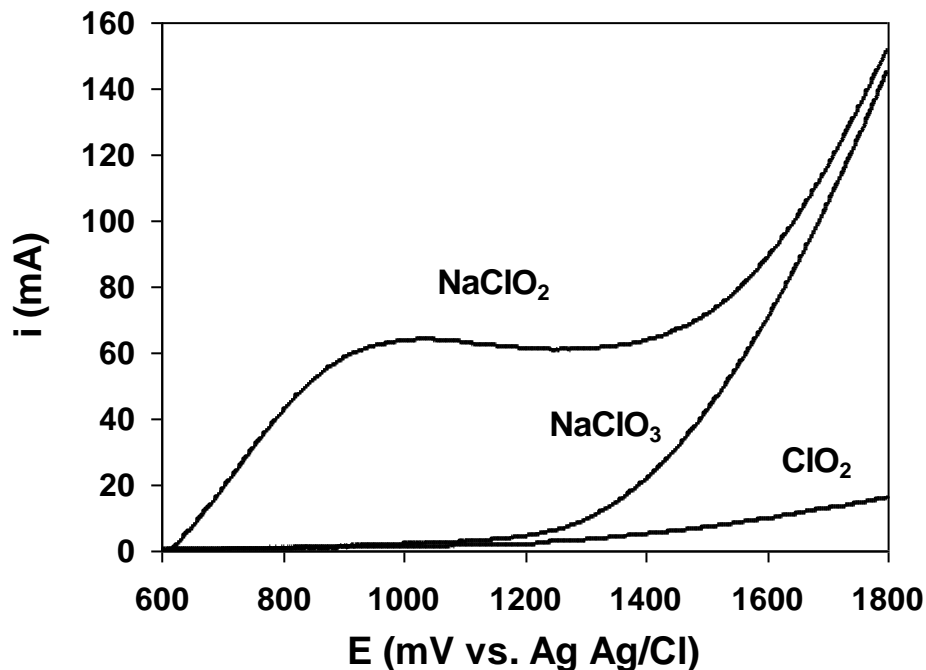
Figure 3. Anodic LSV for 0.01 M $NaClO_2$, 0.01 M $NaClO_3$, and 0.0013 M ClO_2. $v = 200$ mVs^{-1}. [19]

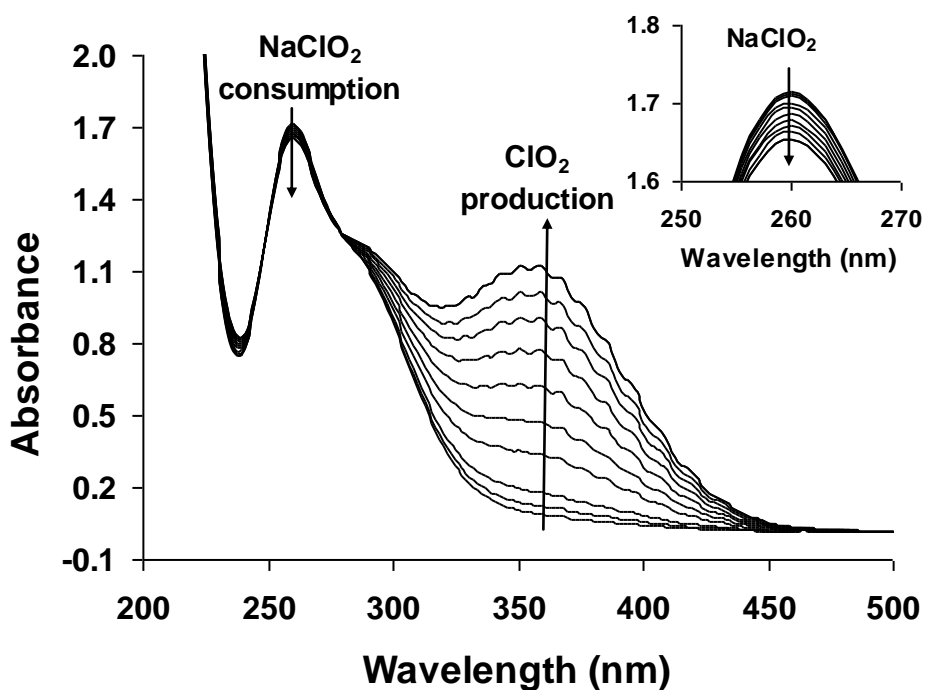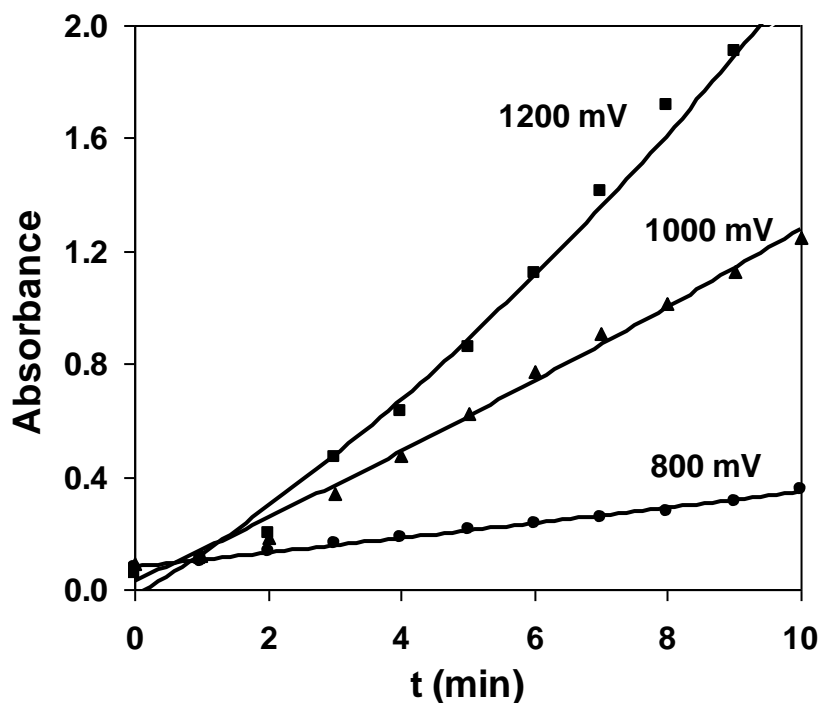**Figure 4.** Spectroelectrochemical response of 0.01 M $NaClO_2$ with time. $E_{anode} = 1000$ mV vs. Ag/AgCl.

With this information, three potentials were selected for the spectroelectrochemical study in the $NaClO_2$ oxidation range: 800, 1000 and 1200 mV vs. Ag/AgCl. ClO_2 was indeed produced at these

potentials and its evolution was monitored in situ and in real time through its characteristic absorbance peak at 359 nm (Figure 4).[19] The ensuing consumption of $NaClO_2$ was evidenced through the decrease of its 260 nm absorbance peak (see the insert in Figure 4). As expected, the production of ClO_2 increased with potential in this range (Figure 5).

Figure 5. Anodic production of ClO_2 from 0.01 M $NaClO_2$ as a function of time at different potentials. (Absorbance measured at 359 nm).[19]

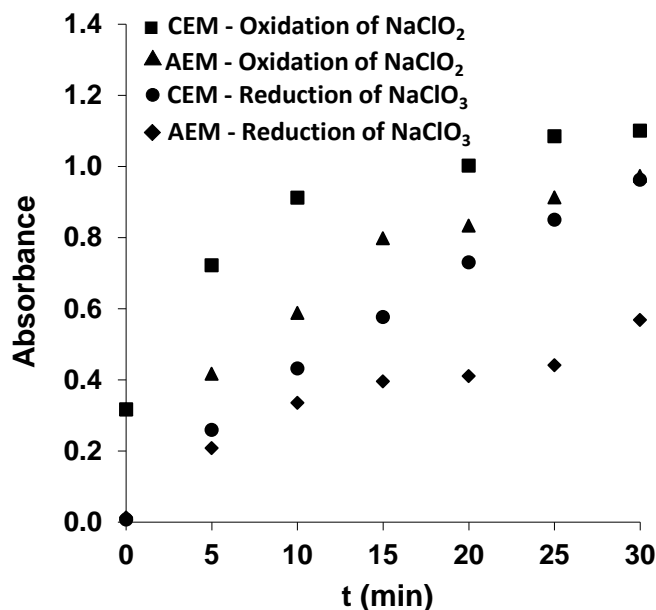*3.2 Indirect reduction of $NaClO_3$*

The cathodic production of ClO_2 from $NaClO_3$ was evaluated and monitored at 300, 500 and 800 mV vs. Ag/AgCl in highly acidic media.[20] The point at 300 mV was found to be unsuitable for this purpose, while a potential of 800 mV gave the highest yield.
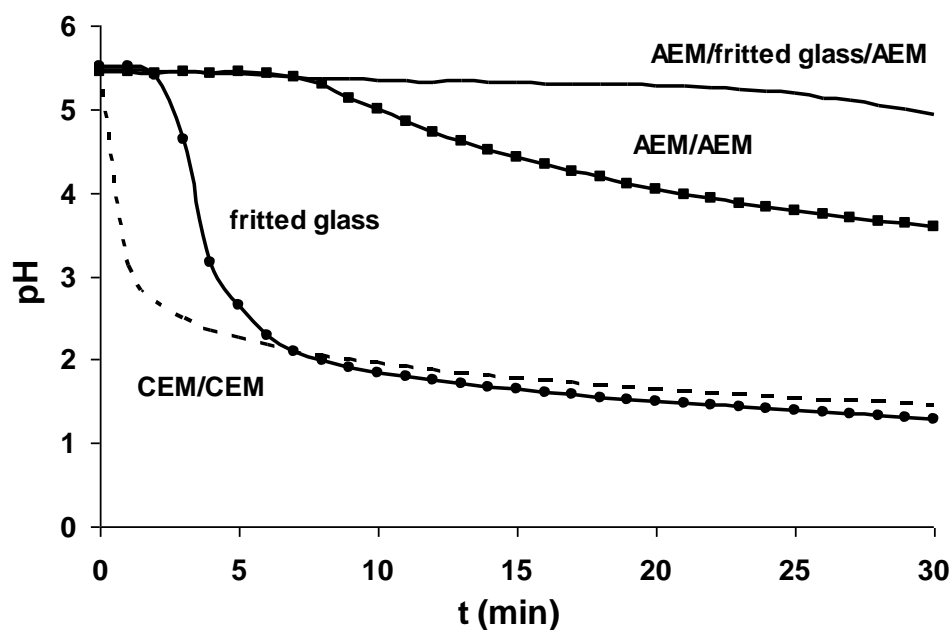
3.3 Analysis of possible separation schemes

In order to probe the conditions for the convergent production of ClO_2 at both electrodes, the (highly acidic) catholyte and the anolyte must be separated to prevent their interaction, since passage of H_3O^+ from the former to the latter is known to chemically produce ClO_2. To this end, different membrane arrangements were tested to monitor the production of ClO_2 at both electrodes according to the scheme shown in Figure 2. A comparison of experiments involving a single membrane arrangement revealed that the mobility of cations through a CEM was more effective for the production of ClO_2 than that of anions through an AEM (Figure 6). In order to ascertain whether part

of this production could be due to the undesired acidification of the anolyte from the catholyte, additional separation arrangements involving fritted glass, CEM, and AEM were tested by monitoring possible changes (caused by proton diffusion) on the pH of distilled water placed in the anolyte vs. time.
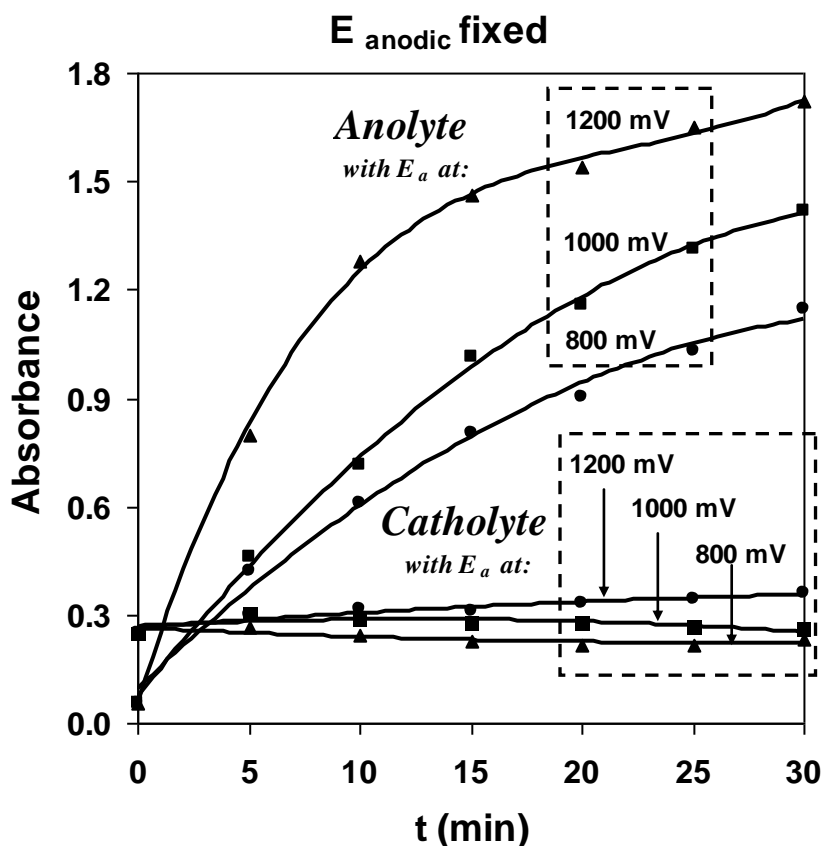

Figure 6. Production of ClO_2 in a divided cell with a single membrane arrangement. Oxidation: 0.01 M ClO_2^- direct oxidation at 1000 mV vs. Ag/AgCl (catholyte: 0.1 M Na_2SO_4). Reduction: indirect reduction at 800 mV vs. Ag/AgCl of 0.006 M ClO_3^- in 7.36 M H_2SO_4 (anolyte: 0.1 M Na_2SO_4). Absorbance measured at 359 nm.[19]

Figure 7. Anolyte pH as a function of time for different separators and combinations. Catholyte: 7.36 M H_2SO_4.

The results with four different arrangements (AEM/AEM, AEM/fritted glass/AEM, CEM/CEM and fritted glass alone) are shown in Figure 7.[19] The CEM/CEM and fritted glass-alone arrangements allowed the undesired passage of H_3O^+ early in the reaction, whereas the arrangement of AEM/fritted glass/AEM was significantly effective in preventing this passage during the working timeframe (i.e., a ΔpH of only ca. 0.5 units was observed after 30 min). The AEM/AEM exhibited intermediate results between these two extremes. Since these last two arrangements were the most satisfactory for the present purpose, they were further tested by placing a $NaClO_2$ solution in the anodic compartment and monitoring any possible production of ClO_2 due to H_3O^+ leakage from the catholyte. In agreement with the above results, the AEM/AEM arrangement promoted the chemical production of a substantial amount of ClO_2, whereas this was barely noticeable in the AEM/fritted glass/AEM system. Therefore, this last arrangement was selected for the study of the convergent production as described below.
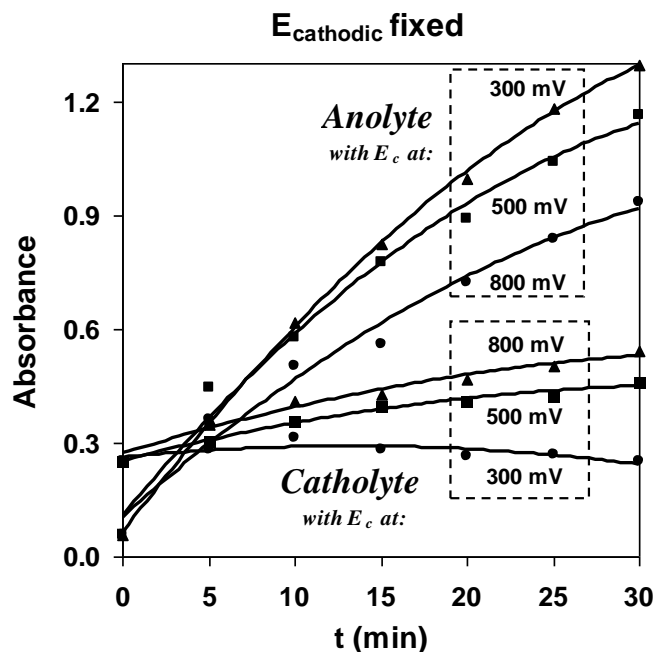
3.4 Convergent production of ClO_2

Figure 8. Convergent production of ClO_2 at fixed anodic potentials. Anolyte: 0.01 M ClO_2^-, catholyte: 0.006 M ClO_3^- and 7.36 M H_2SO_4. (Absorbance measured at 359 nm).[19]

The convergent production of ClO_2 was studied by fixing the potential of one electrode and monitoring that of the other electrode, as well as by monitoring the ClO_2 production at both sides. Figure 8 shows both ClO_2 absorbances obtained by fixing the *anodic* potential at the different values

discussed earlier (i.e., 800, 1000 and 1200 mV vs. Ag/AgCl). The anodic production was favored as the potential increased beyond the rest potential of each individual anodic solution, whereas the cathodic production was essentially negligible. The potentials attained by the cathode oscillated between 100 and 200 mV vs. Ag/AgCl, which explains the low yields obtained at this side.[20] Analogously, the results obtained when fixing the *cathodic* potential at 300, 500 and 800 mV vs. Ag/AgCl are given in Figure 9.

Figure 9. Convergent production of ClO_2 at fixed cathodic potentials. Anolyte: 0.01 M ClO_2^-, catholyte: 0.006 M ClO_3^- and 7.36 M H_2SO_4. (Absorbance measured at 359 nm).[19]

In agreement with previous results,[20] the cathodic production was favored as the potential approached the rest potential, whereas the anodic production behaved in the opposite manner. This last result was due to the distribution of potential at the anode when the cathodic potential was fixed, i.e., the higher the cathodic potential, the smaller the anodic potential. Table 1 shows the ClO_2 percentage yields, calculated as follows:[19]

$$\eta = [(\text{final moles of } ClO_2 - \text{init. moles of } ClO_2, \text{ if any})/\text{max. stoichiom. moles of } ClO_2] \times 100 \quad (1)$$

Table 1. Conversion percentages for the convergent production of ClO_2. (Total reaction time for each run = 30 min).

Fixed anodic potential				Fixed cathodic potential			
E vs. Ag/AgCl	Anodic conversion, %	Cathodic conversion, %	Total conversion, %	E vs. Ag/AgCl	Anodic conversion, %	Cathodic conversion, %	Total conversion, %
800 mV	0.06	6.45	6.51	800 mV	1.43	5.20	6.63
1000 mV	0.27	8.08	8.35	500 mV	1.02	6.57	7.59
1200 mV	0.53	9.85	10.38	300 mV	0.31	7.34	7.65

4. CONCLUSIONS

The production of ClO_2 at both electrodes of an electrochemical cell can be achieved using a divided cell. An anion exchange membrane/fritted glass/anion exchange membrane combination prevents proton migration from the anolyte into the catholyte, which would lead to the undesired chemical production of ClO_2. The generation of ClO_2 and the disappearance of ClO_2^- in the anolyte are simultaneously monitored in situ by a spectroelectrochemical arrangement. The corresponding yields are highly dependent on the applied potential: the cathodic production is favored as the potential approaches the rest potential of the catholyte, whereas the anodic production behaves in the opposite manner.

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