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Electrosynthesis of hydrogen peroxide via the reduction of oxygen assisted by power ultrasound

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Abstract

The electrosynthesis of hydrogen peroxide using the oxygen reduction reaction has been studied in the absence and presence of power ultrasound in a non-optimized sono-electrochemical flow reactor (20 cm cathodic compartment length with 6.5 cm inner diameter) with reticulated vitreous glassy carbon electrode (30 x 40 x 10 mm, 10 ppi, 7 cm^2 cm^{-3}) as the cathode. The effect of several electrochemical operational variables (pH, volumetric flow, potential) and of the sono-electrochemical parameters (ultrasound amplitude and horn-to-electrode distance) on the cumulative concentration of hydrogen peroxide and current efficiency of the electrosynthesis process have been explored. The application of power ultrasound was found to increase both the cumulative concentration of hydrogen peroxide and the current efficiency. The application of ultrasound is therefore a promising approach to the increased efficiency of production of hydrogen peroxide by electro-synthesis, even in the solutions of lower pH (< 12). The results demonstrate the feasibility of at-site-of-use green synthesis of hydrogen peroxide.

Keywords: hydrogen peroxide, sono-electrochemistry, reticulated vitreous glassy carbon, green synthesis

1. Introduction

Hydrogen peroxide is an environmental friendly oxidizing agent with many uses in organic and inorganic synthesis, waste water treatment and pulp industry [1, 2]. A large number of synthetic chemists seeking *greener* syntheses are turning toward hydrogen peroxide based oxidations, since water is the sole by-product of these oxidations [3-5]. Moreover expensive catalysts and solvents may be avoided while the need for costly organic peroxides or chlorine based oxidations can be eliminated.

Hydrogen peroxide is made commercially *via* anthraquinone reduction known as the ‘AQ-process’. This involves the hydrogenation, for example, of 2-alkyl-9,10-anthraquinone (with a catalyst such as nickel or palladium) forming the corresponding hydroquinone and oxidation with oxygen (usually air) to yield hydrogen peroxide and reforming the starting anthraquinone. Commonly the anthraquinone is dissolved in a solvent or solvent mixture for hydrogenation, oxidation and extraction. Due to the differing solubility of the quinone and hydroquinone species, solvent mixtures are commonly employed. The sole electrochemical process competitive to ‘AQ’ process is the Dow Process developed in association with Huron Technologies Inc. The major disadvantages for the widespread commercialisation of the direct oxygen electroreduction technology are the high alkalinity and high, 1.7-1.8 $NaOH/H_2O_2$ weight ratio [6]. Therefore, there is a continuous search for an improved electrochemical synthesis of hydrogen peroxide from oxygen in aqueous media [7]. However, production of hydrogen peroxide *via* electroreduction of oxygen has two main drawbacks: the low solubility of oxygen in water and the sluggish kinetics of the electrochemical reduction of oxygen [8] with low current efficiencies.

To enhance the oxygen electroreduction to hydrogen peroxide at low pH, i.e. less than 12, previous research has mainly focused on electrode materials [9-11], influence of the pH [12], use of surfactants [13], mediated electro-reduction using 2-ethyl 9,10-anthraquinone [14,15], and use of electrodes modified with electrocatalytic materials [16-21]. Due to the slow kinetics of the oxygen reduction and the low solubility of the oxygen in aqueous solution, three dimensional electrodes with a high ratio of surface area to volume in flow cells, have been commonly used in the electrosynthesis of hydrogen peroxide. Among them, reticulated vitreous carbon (RVC) has received special attention

[22] with studies again addressing the influence of the pH [6, 12], the use of surfactants [6] and the use of mediators [23] to increase the rate of the electron transfer process.

Due to the low solubility of the oxygen in aqueous solutions, the electrochemical synthesis of hydrogen peroxide from the reduction of oxygen will likely have a low synthetic efficiency if this is not carried out at high forced convection conditions. The depletion of the oxygen at the electode requires a continous supply from the bulk solution in order to mantain the oxygen concentration at electrode surface as high as possible. The influence of ultrasound on the electrochemical behaviour of different systems is a now well understood field of reserach [24]. Thus, effects have been found on activation of the electrode surface [25], on adsorption processes [26], modifications of mechanisms due to radical generation [27] and also the increase the mass transport of electroactive species to the electrode [28]. In the case of the oxygen electro-reduction, the influence of the ultrasound has been analyzed by voltammetric studies using unmodified [29] and modified electrodes [18, 30-32].

One potential approach to the green synthesis of hydrogen peroxide synthesis is from applying sono-electrochemistry where it is envisaged that large amounts of hydrogen peroxide would be quickly and economically produced from the enormously enhanced mass transport regime under ultrasound. The physical principles underlying the simultaneous application of ultrasound and electrochemistry have been well understood over the last decade and it is expected that very substantial amounts of hydrogen peroxide can be generated in this way using air as a feedstock.

In the present work the electrosynthesis of hydrogen peroxide *via* the oxygen reduction reaction has been studied at pH 10 and pH 13 in the presence and absence of ultrasound using a non-optimized electrochemical flow reactor with RVC as the cathode. The influence of several classical electrochemical operational variables (pH, volumetric flow, potential) and of the sonoelectrochemical parameters (ultrasound amplitude and horn-to-electrode distance) on the cumulative concentration of hydrogen peroxide and current efficiency of the electroreduction of oxygen to hydrogen peroxide has been investigated.

2. Experimental

2.1 Reagents and chemicals

All chemicals used in this work were of analytical grade and used as received from Aldrich without further purification. Two different catholytes were used; a boric acid / sodium hydroxide buffer for pH 10.0 and sodium hydroxide solution for pH 13 with 0.1 M solution of sodium hydroxide used as an anolyte. All solutions were prepared with deionised water of resistivity not less than 18.2 MΩ cm (Vivendi Water System UK). Pure oxygen (BOC, Guildford, Surrey, UK) was bubbled in (P= 0.1 MPa) prior (more than two hours) to and during the electrochemical and sono-electrochemical experiments. Note that no peroxide stabilization agent was added to the catholyte.

2.2 Electrochemical reactor

A divided flow cylindrical cell was used for the electrolysis with a reticulated vitreous carbon (30 x 40 x 10 mm, Duocel Reticulated Vitreous Carbon 10 ppi, 7 cm^2 cm^{-3}) as a working electrode. The counter electrode was nickel gauze, with a saturated calomel electrode (Radiometer, Denmark) completing the circuit. A plastic tube Luggin capillary entered the three dimensional cathode *via* a hole drilled through the wall of the cell. The volume of the anolyte was 0.5 dm^3 and, in most experiments the volume of the catholyte was 1.25 dm^3 and 3 dm^3. The catholyte volumetric flow rate was ranged between 70 and 300 dm^3 h^{-1}. A cationic exchange membrane Sibron MC3470 (IONAC, Sybron Chem. Inc. USA) was used as a separator. The experimental apparatus is shown in the **figure 1**. Both catholyte and anolyte (each one in its own loop) were circulated trthrough its electrode comparment via a pump and external reservoir in the typical way of the flow electrochemical reactor with recirculation. The cathodic compartment length of the cell is 20 cm and the anodic compartment length is 4 cm while the inner diameter of the cell is 6.5 cm.

2.3 Instrumentation

Controlled potential electrolysis was carried out on a PGSTAT30 potentiostat (Autolab, Eco Chimie, Utrecht, The Netherlands). For the sonovoltametric study, an ultrasonic horn, model CV 26 (Sonics and Materials Inc.USA), operating at a frequency of 20 kHz and fitted with a 3mm diameter titanium alloy microtip was used (Jencons, Leyton Buzzard, UK). In the flow cell sonoelectrochemical experiments, the ultrasound field is applied using a 20 kHz Ultrasonic Processor UIP (1000 W) supplied by Dr. Hielscher GmbH, fitted with a 34 mm diameter titanium alloy tip. The working electrode was placed directly opposite the ultrasound horn in a face-on arrangement with a distance between them being an operational variable under study. Temperature was kept constant at 21 ± 2 ^{o}C throughout all electrochemical and sonoelectrochemical experiments.

The cumulative concentration of hydrogen peroxide was determined by spectrophotometry (to within ± 3%) using samples taken from the cathodic circulation tank. The colorimetric procedure used is based on the detection of iodine generated in a degassed iodide solution after the *in situ* reaction with hydrogen peroxide [33]. After the long term electrolysis, the electrolyte was allowed to flow through the system during one hour and the concentration of hydrogen peroxide did not change more than 3% during this time.

3. Results and discussion

3.1 Voltammetry study

Prior to the study of the process using a flow-cell, a voltammetry study was carried out at pH 10 using RVC samples as working electrode. The objective of this study is located the potentials at which oxygen is not reduced and those at which it is reduced (i) under electrode kinetic control and (ii) under transport control. A three electrode arrangement was used in the electrochemical cell and two different size of working electrode were studied. In a first step, a 10 x 10 x 10 mm reticulated vitreous carbon was used as a working electrode, the counter electrode was platinum wire around the working electrode and a saturated calomel electrode as a reference electrode. This system was used to analyze the influence of the ultrasound field provided by a 20 kHz ultrasound horn, located at "face on" configuration delivering 10% of amplitude. **Figure 2a** shows the cyclic voltametry, v=10 mV/s, in absence of oxygen at silent conditions (curve a), and in presence of oxygen in silent conditions (curve b) and in presence of ultrasound (curve c). The wave related to the oxygen reduction in silent conditions (curve b) presents a peak located at -0.4 V vs SCE, a potential value close to that obtained with other carbonaceous substrates [31] at similar experimental conditions. Under ultrasound, note the increase in current density and a possible mass- transport limited current density arising form enhanced mass transport at more negative potentials than the peak potential in silent conditions, E_{peak} = -0.4 V vs SCE.

In order to analyze the voltametric behaviour with larger electrodes, close to the size used in the flow cell, a 60 x 50 x 10 mm reticulated vitreous carbon was used also as a working electrode. With this large working electrode, a large platinum wire counter electrode was positioned around the working electrode in order to assure a high symmetry in the current field. **Figure 2b** shows the voltammetric response, 10 mV/s, in absence (curve a) and presence (curve b) of oxygen in silent conditions. The peak is located at -0.49V vs SCE, and the halfwave potential is located at -0.37 V vs SCE. It is worth noting that, despite the increase in the size of the working electrode and its implications for the homogeneity of the potential distribution over the 3D electrode surface, the voltammetric peak potential is almost unchanged from that obtained with the smaller working electrode sizes (Figure 2a).

3.2 Study under silent conditions

3.2.1 Study at pH 13

The electrosynthesis of hydrogen peroxide under quiescent conditions in the electrochemical flow reactor was first investigated. In all experiments, the catholyte of 1.25 dm^3 volume was continuously saturated with oxygen introduced in the recirculation tanks with periodic hydrogen peroxide concentration monitored colorimetrically. The electrosynthesis of hydrogen peroxide was studied in a pH 13 solution where the hydrogen peroxide exists as HO_2^- so that loss of hydrogen peroxide *via* decomposition to water and oxygen is reduced. The accumulation of hydrogen peroxide with time within the catholyte for electrosynthesis carried out in pH 13 solution at different potentials is shown at **figure 3**. It can be seen that the concentration of hydrogen peroxide increases linearly with time, with the rate of formation of hydrogen peroxide being higher at more negative potentials. The cumulative concentration of the hydrogen peroxide was shown to be strongly dependent of the volumetric flow rate as can be seen at **figure 3**. On the other hand, the current efficiency, defined as the ratio of the charge used to form hydrogen peroxide by Faraday's law to the total charge passed, was not strongly influenced by the potential in the range – 0.6 to – 1.2 V *vs.* SCE or the volumetric flow rate in the range 70 to 300 dm^{3}h^{-1}. The current efficiency was in the range 30 - 45% for hydrogen peroxide electrosynthesis at volumetric flow rate of 70 dm^{3}h^{-1}, with values of 40 - 60% obtained for volumetric flow rate of 300 dm^{3}h^{-1}. Also, the existence of "induction time", i.e. an initial period of time when the current efficiency is low, has been observed.

3.2.2. Study at pH 10

Next we examined the electrosynthesis of hydrogen peroxide under silent conditions in oxygen – saturated solution of pH 10 value. The experiments were run under the same conditions described above for electrosynthesis of hydrogen peroxide in catholyte of pH 13, and a summary of the results is shown in **figure 4**. The concentration of hydrogen peroxide increased again with time and higher cumulative concentrations of hydrogen peroxide were obtained at the higher volumetric flow rate. However, the current efficiency of the hydrogen peroxide electrosynthesis at pH 10 was found to be a function of the potential. It was observed that the current efficiency decreases at more negative potentials with values ranging from close to 100% for the electroreduction of oxygen at -0. 4 V *vs.* SCE to values as low as 20% for the reduction at - 1.0 V *vs.* SCE.

The comparative analysis of the current efficiency of hydrogen peroxide electrosynthesis at two different catholyte volumetric flow rate, 70 dm^3h^{-1} and 300 dm^3h^{-1} showed that the influence of the flow rate is more manifested at potentials more positives (-0.6 V vs SCE). The current efficiency for electrosynthesis of hydrogen peroxide at - 0.6 V *vs.* SCE was found to be *ca.* 55% at 300 dm^3h^{-1} volumetric flow rate, while it was almost half less at 70 dm^3h^{-1} volumetric flow rate. However, the effect of flow rate on current efficiency at more negative potentials is practically negligible and the value of *ca.* 20% was obtained for both volumetric flows-rate for electrosynthesis at - 1.0 V *vs.* SCE.

3.3 Study under ultrasonic conditions

We turned to investigation of the electrosynthesis of hydrogen peroxide under the ultrasound. The electrode potential was kept constant at - 1.0 V *vs.* SCE throughout all sono-electrochemical measurements. It must be highlighted that no electrode damage was detected during the study. Note that the electrosynthesis of hydrogen peroxide shows poor current efficiency at this potential under the quiescent conditions (see above).

3.3.1. Chronoamperometric studies. Influence of the ultrasound amplitude and the horn-electrode distance

Chronoamperometric studies of the electrosynthesis of hydrogen peroxide under the ultrasound were performed in a flow cell with the catholyte of pH 13 value. The horn-to-electrode distance was kept constant at 5.6 cm throughout the whole set of measurements while the ultrasound power was increased from 0 to the maximum value. The potential step experiments, **figure 5**, were run with two different catholyte volumetric flow rates: 70 and

200 dm^3h^{-1}. A large enhancement in current is observed as the ultrasound amplitude increases compared to the ones obtained under quiescent conditions; the increase was found to be more notable for lower volumetric flow rate. The reduction current of electrosynthesis with volumetric flow rate of 70 dm^3h^{-1} and 200 dm^3h^{-1} increased 2.6 and 1.2 times respectively when ultrasound of maximum power was applied compared to the currents obtained with no ultrasound applied. Note that after the ultrasound horn is switched off, the current attains the initial value in silent conditions before application of ultrasound. When the experiments were repeated in solution of pH 10 value, similar qualitative enhancement in current to that reported above for the pH 13 was observed with the 2.2 times increase in current for lower flow rate when ultrasound of maximum power was applied compared to the obtained silent current.

Next, a different horn-to-electrode distance was examined. The horn was placed at 1.5 cm distance from the RVC electrode and electrosynthesis of hydrogen peroxide investigated in pH 10 solution. Somewhat different results were obtained at this horn-to-electrode distance compared to that obtained using a greater distance. The increase in the current under ultrasound was to some extent more pronounced and the ratio of 'ultrasound' to silent current was found to be higher, 2.6 and 1.7 times for volumetric flow rates of 70 and 200 dm^3h^{-1} respectively. The silent current after the ultrasound application was found to be 25% higher than silent current before application of ultrasound.

3.3.2. Controlled potential electrolysis. Influence of the pH

Next, the effect of ultrasound on the cumulative concentration of hydrogen peroxide and current efficiency of the hydrogen peroxide electrosynthesis was studied. The electrosynthesis of hydrogen peroxide was first examined in a flow reactor with a pH 10 solution of 3 dm^3 volume used as catholyte. The electrosynthesis with two different catholyte volumetric flow rates: 70 and 200 dm^3h^{-1} were examined. **Figure 6** shows the cumulative concentration of hydrogen peroxide *versus* time in the presence and absence of ultrasound. The cumulative concentration at any time is higher as the ultrasound amplitude increases. For both volumetric flow rates, the presence of ultrasound increases the cumulative concentration of hydrogen peroxide, even a higher flow rates where the increase in the current under ultrasound was not very pronounced. The current efficiency in silent conditions was found to be low, close to 20%. However, the current efficiency increased significantly when ultrasound is applied during electrosynthesis, see **figure 7**. The usual explanation for an increased current efficiency under insonation is that the ratio of faradaic current to background increases as a result of the increased mass transport improving the former but not changing the latter. This increase in the current efficiency is more manifested at low volumetric flow rates. For electrosynthesis of hydrogen peroxide with the higher catholyte volumetric flow rates the ultrasound amplitude increases, the current efficiency seems to be independent of the volumetric flow rate. It was also found that, when ultrasound is applied during electrosynthesis of hydrogen peroxide, the "induction time" in the current efficiency curve disappears. This increase in current efficiency of hydrogen peroxide electrosynthesis under ultrasound offers a promising prospect, especially where the conventional electrochemical approaches (low pH and higher electrode potential) does not meet the market demands.

The same study was done at pH 13. Again, the presence of the ultrasound field with increasing power amplitude enhances the electrosynthesis of hydrogen peroxide, not only in the cumulative concentration, but also in the current efficiency of the process. However, these beneficial effects are less pronounced than those obtained at pH 10 and, for example, the "induction time" in the current efficiency curves remains.

Long term electrolysis was carried out to check the hydrogen peroxide synthesis and a linear increase in the cumulative concentration was detected over the whole reaction period of 7 hours.

Several effects of ultrasound related to the electrochemical processes have been reported such as enhancement of the mass transport at the electrode [34], ultrasound-induced surface effects [35] and generation of active radical species [36]. In water, the sonochemical formation of $OH^{\cdot}$ radicals is followed by recombination of hydrogen peroxide [37] or by the activation of carbon surfaces [38]. The influence of the ultrasound on the rates of heterogeneous electron transfer is largely indirect and due to mass transport effects [28].

Assuming that ultrasound improves only the mass transport conditions, the observed less pronounced benefits of the ultrasound applied at higher volumetric flow rates are likely due to the fact that the mass transport contribution from the ultrasound field is lower or disturbed as the volumetric flow rates increase. This is consistent with the fact that the limiting current observed in the presence of ultrasound is found to increase with the magnitude of the ultrasound intensity applied to the system, as reported elsewhere [34]. A quantitative model has been proposed to parameterize the mass transport to insonated macrodisc electrodes. This assumes that the application of power ultrasound results in a truncated or thinned Nerst diffusion layer [28] and it has been found experimentally that the diffusion layer thickness is controlled by both difusion and convection [39]. In the case of the insonated electrode, acoustic steaming contributes significantly to this convective flux [40] so that the influence of the ultrasound is greater at lower volummetric flow rates.

Optimization of the cell geometry, study relative configuration emitter surface-electrode and the correlation between structural properties of the 3D electrode with ultrasound field are the next points to further develop in order to increase the efficiency of the process.

4. Conclusions

A study of the influence of ultrasound on the electroreduction of oxygen to hydrogen peroxide was carried out in a non-optimized electrochemical flow cell using reticulated vitreous carbon as a working electrode. The examination was performed in pH 13 where HO_2^- anion is known to be stable, as well as in pH 10 where electrosynthesis of hydrogen peroxide shows poor efficiency. The application of ultrasound during electrosynthesis was found to enhance both the cumulative concentration of hydrogen peroxide and the current efficiency of the process. The current efficiencies of *ca.* 60% were reached with the application of ultrasound in solutions of pH 10, where the silent electrochemical synthesis had current efficiency of 20% or less. This improvement can be related to an enhancement in the mass transport under ultrasound. The improvements of electrosynthesis of hydrogen peroxide in solutions of pH 10 under ultrasound compared to quiescent conditions have shown that the application of ultrasound is a promising approach to electrosynthesis of hydrogen peroxide in non-high alkaline aqueous media. This is of great significance for *in situ* production of hydrogen peroxide for use in both organic electrosynthesis and degradation of organic effluents.

Future work on the optimization of the electrochemical flow cell parameters that would further increase the cumulative concentration and improve the current efficiency of the electrosynthesis of hydrogen peroxide is planned.

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6. References

[1] S. D. Burke and R. L. Danheiser, Handbook of Reagents for Organic Synthesis, Oxidizing and Reducing Agents, John Wiley & Sons, Chichester, UK, 1999.

[2] J. S. Do, C. P. Chen J. Electrochem. Soc. 140 (1993) 1632-1637

[3] K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, J. Org. Chem. 61 (1996) 8310-8311.

[4] K. Sato, M. Aoki, J. Takagi, R. Noyori, J. Am. Chem. Soc. 119, (1997) 12386-12387.

[5] K. Sato, M. Aoki, R. Noyori, Science 281 (1998) 1646-1647

[6] E. L. Gyenge, C. W. Oloman J. Electrochem. Soc. 152 (2005) D42-D53

[7] J. A. Mcintyre *Interface* 4 (1995) 29-34

[8] D. Pletcher , F. C. Walsh, Industrial Electrochemistry, second ed., Chapman & Hall, London, 1990

[9]S. M. Golabi, J. B. Raoof, J. Electroanal. Chem. 416 (1996) 75-82.

[10] R. J. Taylor and A. A. Humffray, J. Elecroanal.Chem. 64 (1975) 63-84.

[11] J. Xu, W. Huang, R. L. McCreery, J. Electroanal. Chem.410 (1996) 235-242

[12] A. Alvarez-Gallegos, D. Pletcher, Electrochim. Acta 44 (1998) 853-861

[13]. L. Gyenge, C. W. Oloman J. Appl. Electrochem. 31 (2001) 233-243

[14] A. Huissoud, P. Tissot J. Appl. Electrochem.29 (1999) 11-16

[15] E. L. Gyenge, C. W. Oloman J. Appl. Electrochem. 33 (2003) 655-633

[16] M. S. El-Deab, T. Ohsaka, J. Electroanal. Chem. 553 (2003) 107-115

[17] M. Van Brussel, G. Kokkinidis, A. Hubin, C. Buess-Herman, Electrochim. Acta 48, (2003) 3909-3919.

[18] B. Šljukić, C. E. Banks, R. G. Compton, Phys. Chem. Chem. Phys. 6, (2004) 4034-4041.

[19] A. Sarapuu, K. Vaik, D. J. Schiffrin, K. Tammevestki J. Electroanal. Chem. 541 (2003) 23-29.

[20] K. Vaik, A. Sarapuu, K. Tammeveski, F. Mirkhalaf, D. J. Schiffrin, J. Electroanal. Chem. 564 (2004) 159-166.

[21] K. Tammeveski, K. Kontturi, R. J. Nichols, R. J. Potter, D. J. Schiffrin, J. Electroanal. Chem. 515 (2001) 101-112.

[22] J. M. Friedrich, C. Ponce de León, G. W. Reade, F. C. Walsh J. Electroanal. Chem. 561 (2004) 203-217

[23] A. Huisoud, P. Tissot, J. Appl. Electrochem. 29 (1999) 17-25

[24] (a) D. J. Walton and S. S. Phull, Sonoelectrochemistry, Review in Advances in Sonochemistry, ed. T. J. Mason, JAI Press, 1995, vol. 4. (b) R. G. Compton, J. C. Eklund and F. Marken, Electroanalysis, 9 (1997), 509.

[25] R. G. Compton, J. C. Eklund, S. D. Page, G. H. Sanders, J. Booth, J. Phys. Chem., 98 (1994) 12410,

[26] D. J. Walton, S. S. Phull, A. Chyla, J. P. Lorimer, T. J. Mason, L. D. Burke, M. Murphy, R. G. Compton, J. C. Eklund, S. D. Page, J. Appl. Electrochem. 25 (1995) 1083.

[27] R. G. Compton, F. M. Matysik, Electranalysis 8 (1996) 218.

[28] R. G. Compton, J. L. Hardcastle, J. del Campo, in: P. R. Unwin (Eds.), Encyclopedia of Electrochemistry, Vol. 3, Wiley-VCH, Weinheim, 2003, pp. 290-311

[29] R. G. Compton, F. Marken, C. H. Goeting, R. A. J. McKeown, J. S. Foord, G. Scarsbrook, R. S. Sussmann, A. J. Whitehead, Chem. Commun (Camdrigde) 1988, 1961

[30] A. Salimi, C. E. Banks, R. G. Compton, Phys. Chem. Chem. Phys, 5 (2003) 3988-3993

[31] B. Šljukić, C. E. Banks, S. Mentus, R. G. Compton, Phys. Chem. Chem. Phys. 6 (2004) 992-997

[32] B. Šljukić, C. E. Banks, R. G. Compton, Electroanalysis 17 (2005) 1025-1034

[33] T. J. Mason, Sonochemistry, Oxford Chemistry Primer, 1999

[34] R. G. Compton, J. C. Eklund, S. D. Page, T. J. Mason, D. J. Walton J. Appl. Electrochem. 26 (1996) 775-784

[35] H. Zang, L. A. Coury Jr. Anal. Chem. 65 (1993) 1552-1558

[36] K. Makino, M. M. Mossoba, P. Riesz, J. Phys. Chem. 87 (1983)1369-1377

[37] A. Henglein, Adv. Sonochem. 3 (1997) 17-83

[38] J. Gonzalez-García, J. Iniesta, A. Aldaz, V. Montiel New J. Chem.22 (1998) 343-347

[39] F. Marken, R. P. Akkermans, R. G. Compton, J. Electroanal. Chem. 55 (1996) 415.

[40] F. Marken, J. C. Eklund, R. G. Compton, J. Electroanal. Chem. 39 (1995) 335.

7. Figure Legends

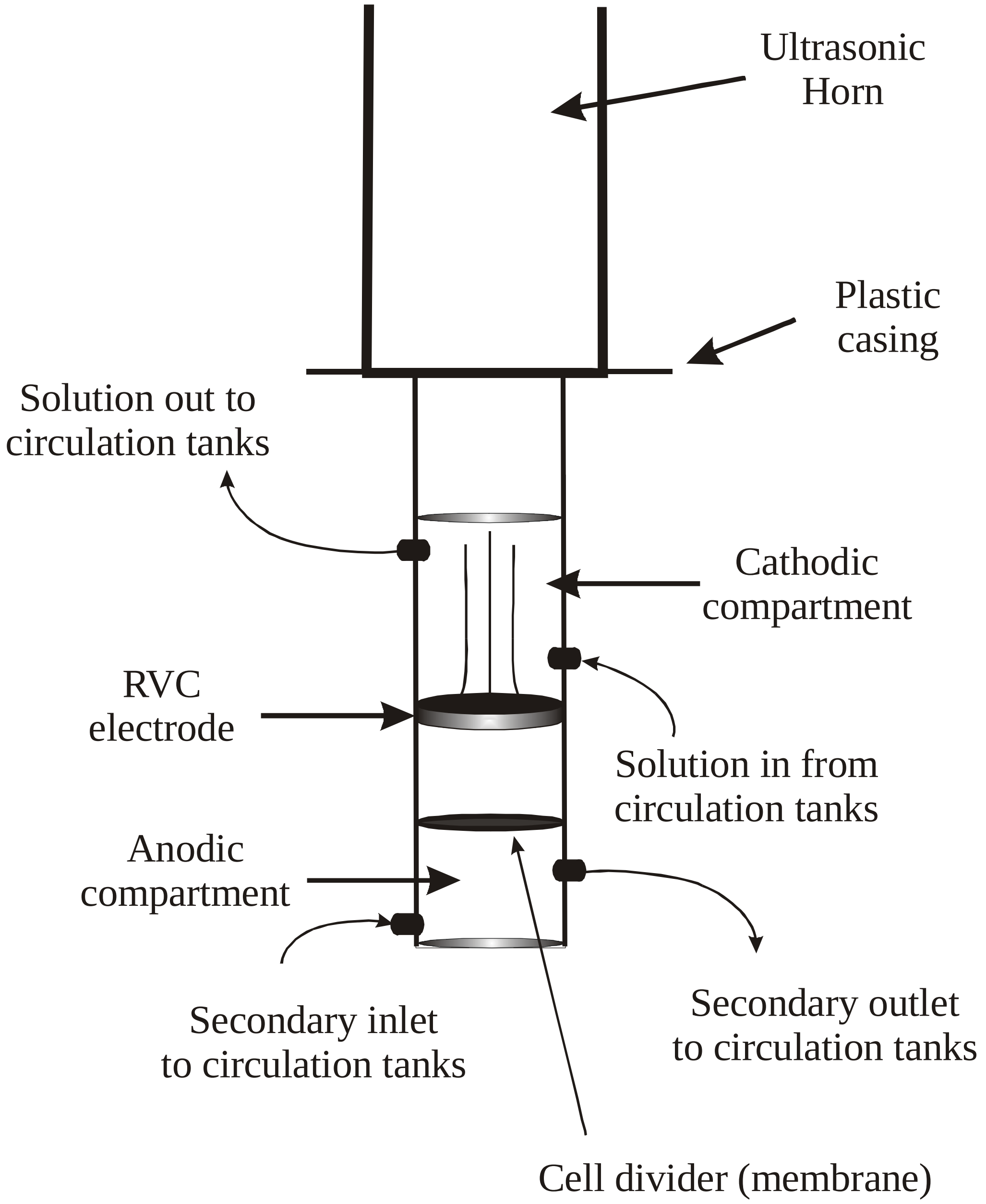


Figure 1: Schematic representation of the sono-electrochemical cell. Note that the cathodic and anodic compartment lengths are 20 cm and 4 cm respectively, while the inner diameter of the cell is 6.5 cm.

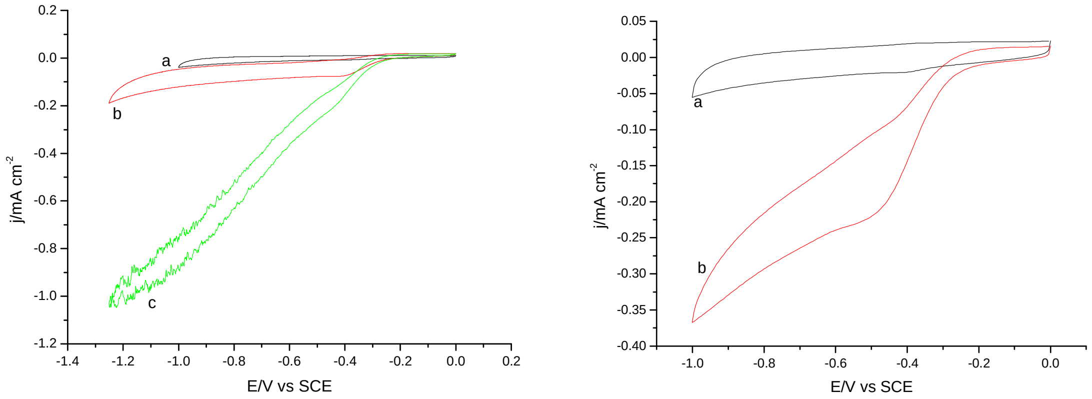


Figure 2: (a) Comparison of cyclic voltammograms for reticulated vitreous carbon (10x10x10 mm) in pH 10 in silent conditions and in the absence (curve a) and in the presence of oxygen at silent (curve b) and ultrasonic conditions (curve c). (b) Comparison of cyclic voltammograms for reticulated vitreous carbon (60x50x10 mm) in pH 10in the absence (curve a) and in the presence of oxygen (curve b).

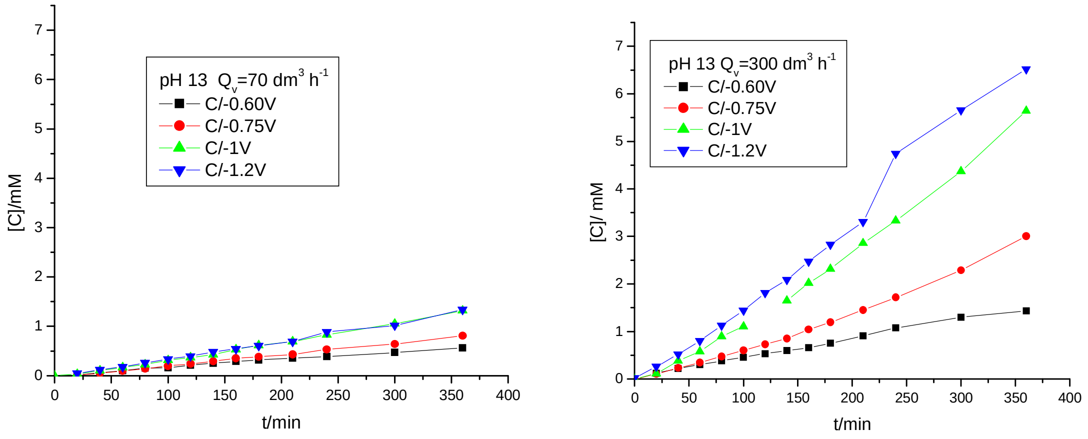
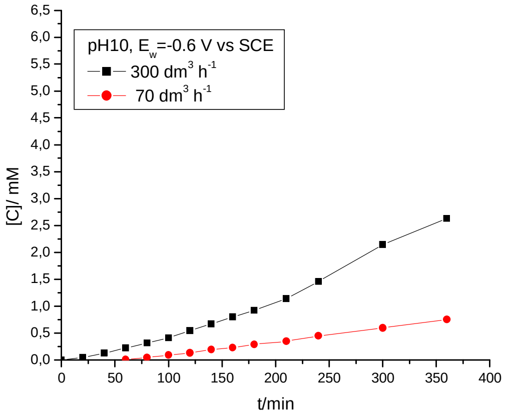


Figure 3: Influence of the electrode potential on the cumulative concentration of H_2O_2 from the electroreduction of O_2 in NaOH (pH 13) at two different flow rates (a) 70 dm^3h^{-1}, (b) 300 dm^3h^{-1}. Temperature 294 K. ■ -0.6 V *vs.* SCE, ● -0.75 V *vs.* SCE, ▲ -1V *vs.* SCE, ▼-1.2V *vs.* SCE. Catholyte volume 1.25 dm^3.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300 dm^3 h^{-1}
70 dm^3 h^{-1}
[C]/ mM
t/min
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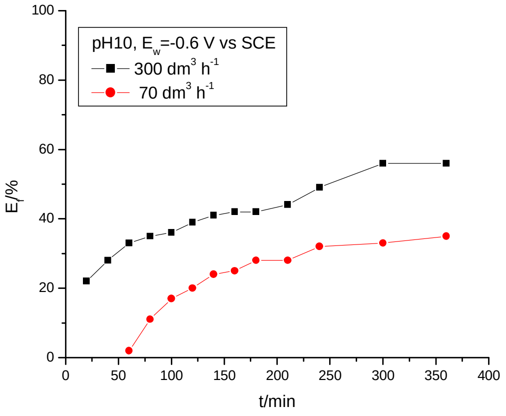
0 50 100 150 200 250 300 350 400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70 dm^3 h^{-1}
E$_f$/%
t/min
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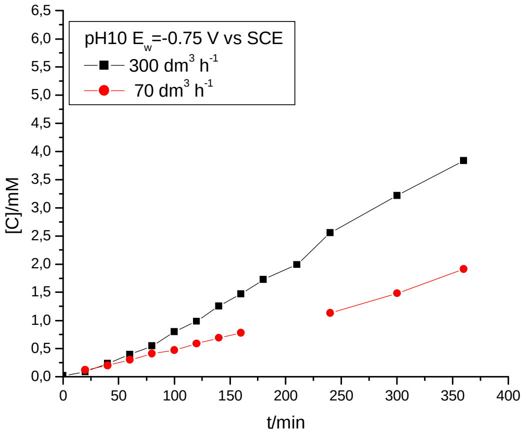
0 50 100 150 200 250 300 350 400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300 dm^3 h^{-1}
70 dm^3 h^{-1}
[C]/mM
t/min
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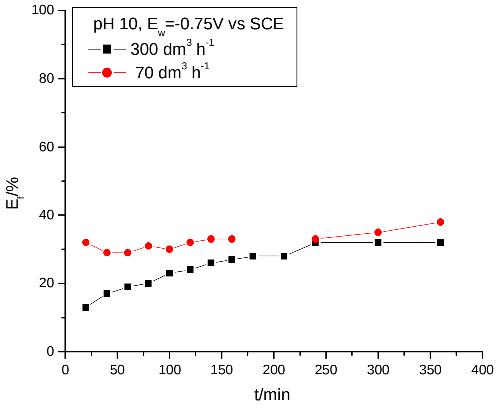
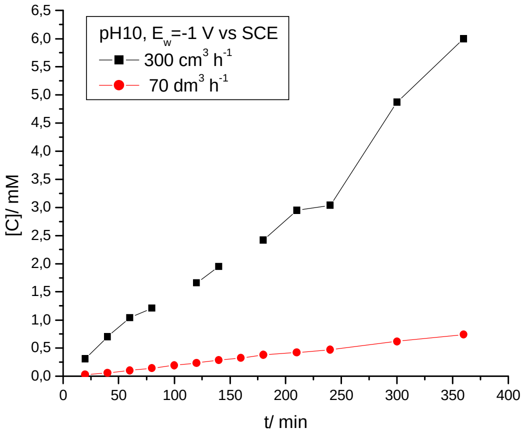

pH 10, E$_w$=-0.75V vs SCE
300 dm^3 h^{-1}
70 dm^3 h^{-1}
E$_f$/%
t/min
0 20 40 60 80 100
0 50 100 150 200 250 300 350 400


pH10, E$_w$=-1 V vs SCE
300 cm^3 h^{-1}
70 dm^3 h^{-1}
[C]/ mM
t/ min
0,0 0,5 1,0 1,5 2,0 2,5 3,0 3,5 4,0 4,5 5,0 5,5 6,0 6,5
0 50 100 150 200 250 300 350 400

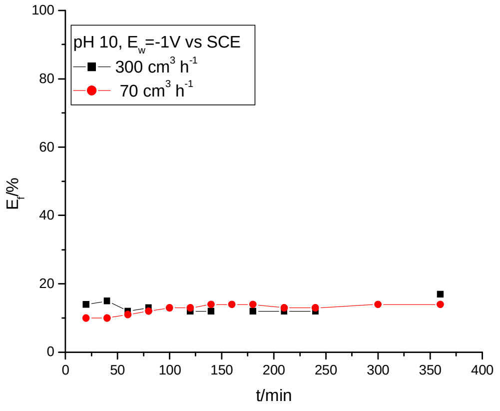

pH 10, E$_w$=-1V vs SCE
300 cm^3 h^{-1}
70 cm^3 h^{-1}
E$_f$/%
t/min
0 20 40 60 80 100
0 50 100 150 200 250 300 350 400

Figure 4: Comparative analysis of the influence of the flow rate on the cumulative concentration and current efficiency of H_2O_2 production for the different electrode potentials studied (- 0.6 V *vs.* SCE, - 0.75 V *vs.* SCE, and - 1V *vs.* SCE) at pH 10. ● 70 dm^3h^{-1}, ■ 300 dm^3h^{-1}. Temperature 294 K. Catholyte volume 1.25 dm^3.

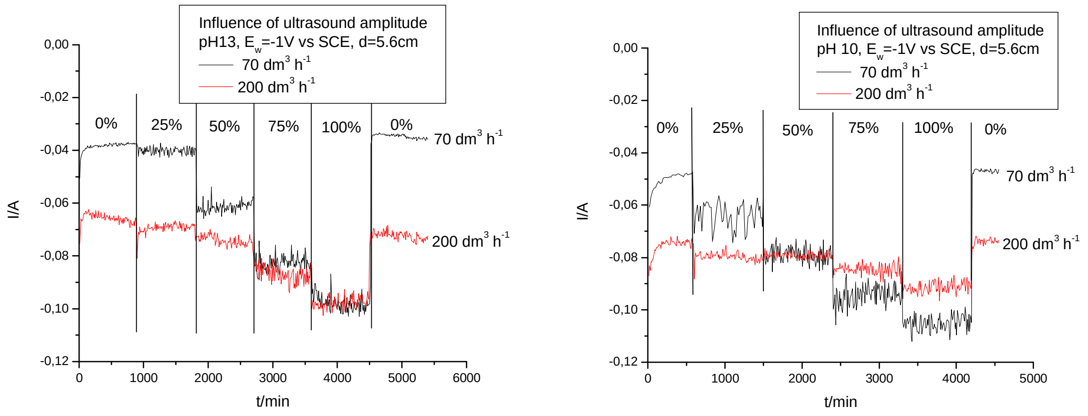


Figure 5: Potential step experiments in the absence and presence of ultrasound (stepped ultrasound amplitude with time) at two different flow rates (70 and 200 dm^3h^{-1}). Distance surface emitter-electrode 5.6 cm (a) pH 13, (b) pH 10.

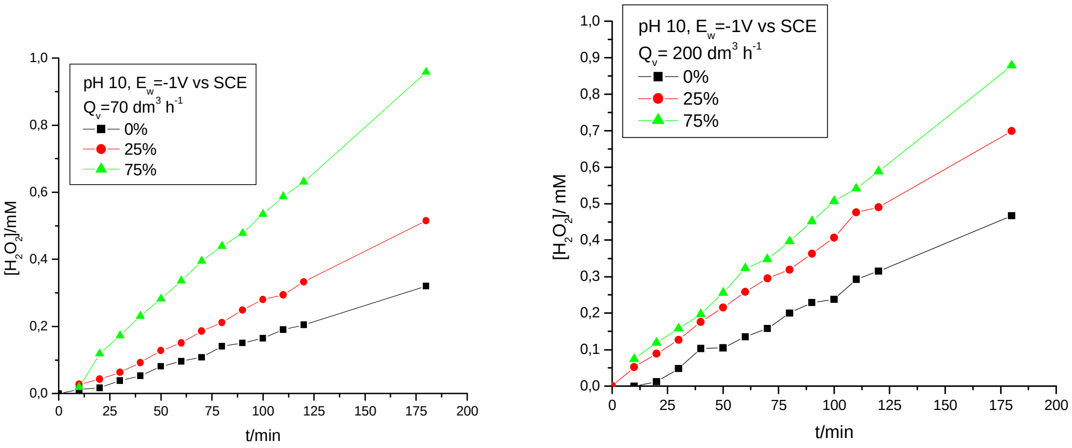


Figure 6: Influence of the ultrasound amplitude on the cumulative concentration of H_2O_2 from the electroreduction of O_2 in NaOH/boric acid (pH 10), Electrode potential -1V *vs.* SCE, at two different flow rates (a) 70 dm^{3}h^{-1}, (b) 200 dm^{3}h^{-1}. Temperature 294 K. ■ 0%, ● 25%, ▲ 75% ultrasound amplitude. Catholyte volume 3 dm^3.

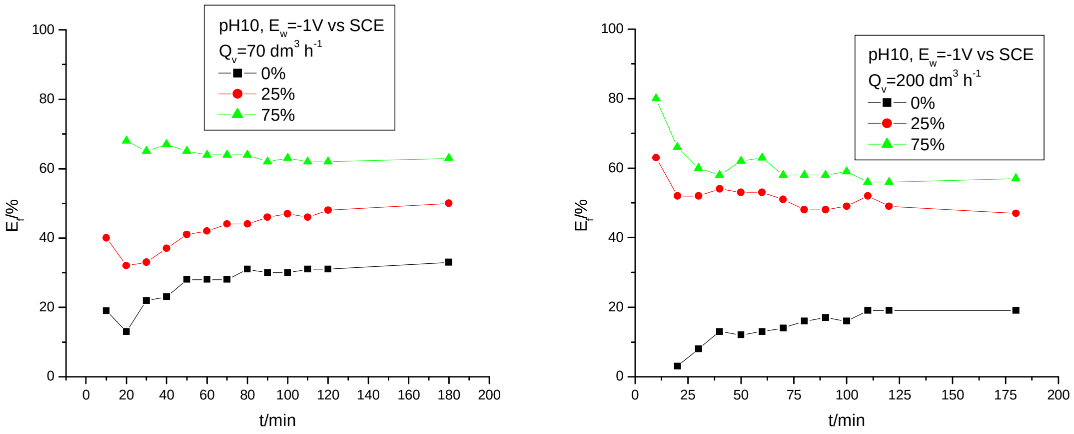


Figure 7: Influence of the ultrasound amplitude on the current efficiency in H_2O_2 production in NaOH/boric acid (pH 10), Electrode potential - 1V *vs.* SCE, at two different flow rates (a) 70 dm^{3}h^{-1}, (b) 200 dm^{3}h^{-1}. Temperature 294 K. ■ 0%, ● 25%, ▲ 75% ultrasound amplitude. Catholyte volume 3 dm^3.