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Effects of the Modification of Gas Diffusion Electrodes by Organic Redox Catalysts for Hydrogen Peroxide Electrosynthesis

Juliane C. Forti,[a] Cristiane E. Venâncio,[b] Marcos R. V. Lanza[a,b] and Rodnei Bertazzoli*,[a]

[a]Departamento de Engenharia de Materiais, Faculdade de Engenharia Mecânica, Universidade Estadual de Campinas,
CP 6122, 13083-970 Campinas-SP, Brazil

[b]Universidade São Francisco, 12916-900 Bragança Paulista-SP, Brazil

Este trabalho apresenta um estudo comparativo da eficiência eletroquímica na eletrogeração de peróxido de hidrogênio *in situ* usando eletrodos da difusão gasosa modificados com os catalisadores orgânicos redox: 2-etilantraquinona, 2-*terc*-butilantraquinona e azobenzeno em meio de 0,1 mol L^{-1} H_2SO_4 + 0,1 mol L^{-1} K_2SO_4, pH = 1. A produção de peróxido de hidrogênio está diretamente relacionada ao potencial aplicado e a concentração dos catalisadores adicionados. A modificação dos eletrodos resultou em um aumento significativo no rendimento de H_2O_2 (30%) alcançando 850 mg L^{-1} e o sobrepotencial da reação de redução do oxigênio foi deslocado para valores menos negativos (400 mV vs Ag/AgCl para os eletrodos modificados com quinonas e 300 mV *vs.* Ag/AgCl para os eletrodos modificados com azobenzeno) comparado ao eletrodo de difusão gasosa não modificado, reduzindo o consumo de energia de 596,5 para 232,4 kWh kg^{-1}. Os resultados indicaram que o melhor eletrodo para a eletrogeração do H_2O_2 é o eletrodo de difusão gasosa modificado com 10% de 2-etilantraquinona, o qual apresentou a melhor relação custo/benefício.

This paper reports a comparative study of the electrochemical performance of *in situ* hydrogen peroxide electrogeneration on gas diffusion electrodes modified by organic redox catalysts 2-ethylanthraquinone, 2-*terc*-butylanthraquinone and azobenzene in medium of 0.1 mol L^{-1} H_2SO_4 plus 0.1 mol L^{-1} K_2SO_4, pH = 1. Hydrogen peroxide generation proved strongly dependent on the applied potential and on the concentration of added catalysts. Electrode modifications led to a significant increase in H_2O_2 yield (30%) reaching 850 mg L^{-1}, and the overpotential for oxygen reduction shifted to less negative values (400 mV vs Ag/AgCl for electrodes modified by quinones and 300 mV vs Ag/AgCl for electrodes modified by azobenzene) compared to noncatalyzed gas diffusion electrodes, resulting in reduced energy consumption of 596.5 to 232.4 kWh kg^{-1}. The results indicated that the best electrode for H_2O_2 electrogeneration is the gas diffusion electrode modified with 10% of 2-ethylanthraquinone, offering the best cost to benefit ratio.

Keywords: hydrogen peroxide, gas diffusion electrodes, 2-ethylanthraquinone, azobenzene, 2-*terc*-butylanthraquinone

Introduction

Hydrogen peroxide is a widely used reagent in processes as bleaching in the textile, pulp and paper industries, food processing, and pharmaceuticals.[1-5] In wastewater treatment, hydrogen peroxide can oxidize organic pollutants to CO_2, offering numerous advantages in terms of treatment rate, cost and availability in comparison to traditional biodegradation methods.[6] Electrochemical technology can be an efficient means of hydrogen peroxide electrosynthesis. The problem of the low solubility of oxygen in aqueous solutions, which limits the reduction reaction by mass transfer rate and, hence, to low limiting current values, can be overcome by the use of three-dimensional electrodes such as gas diffusion electrodes (GDE), which have large areas available for reaction and allow for higher mass transfer rates.[6,7]

In recent times, much interest has focused on the modification of electrodes with organic catalysts for hydrogen peroxide electrosynthesis. Investigations with catalysts of the anthraquinone class to help hydrogen peroxide production have become common (see Table 1). The O_2 reduction reaction mechanism on the surface of anthraquinone-modified electrodes is represented by reactions:[8,9]

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*e-mail: rbertazzoli@fem.unicamp.br

$$Q_{(ads)} + 2e^- + 2H^+_{(aq)} \rightarrow H_2Q_{(ads)} \quad (1)$$

$$H_2Q_{(ads)} + O_{2(aq)} \rightarrow Q_{(ads)} + H_2O_{2(aq)} \quad (2)$$

Oxygen reduction reaction and hydrogen peroxide formation was studied using glassy carbon electrodes modified by physical adsorption of quinone derivatives.[8,14] Electrode modifications by quinones resulted in a shift of the oxygen reduction overpotential to less negative values[8] and a significant increase in current values due to the formation of hydrogen peroxide.[14]

Degrand[17] studied the catalytic reduction of O_2 to H_2O_2 in different pH values using a glassy carbon electrode modified by the adsorption of polymeric-anthraquinone, and observed that the catalytic current value increased with pH.

Oxygen reduction on carbon paste electrodes modified with 1,4-naphthoquinone was studied by Golabi and Raoof[15] at different pH values. These authors observed a gradual increase of the peak cathodic current and a decrease of the peak anodic current as the pH value increased; pH = 8 was adopted as the best value for that study. The optimal condition for O_2 reduction on the surface of carbon paste electrodes modified with 1,4-naphthoquinone was observed to occur at potentials 350 to 550 mV less negative than those of noncatalyzed carbon paste electrodes.[15] It is known that an alkaline medium is more widely used for H_2O_2 production because of OH^- in solution; however, the literature reports that the O_2 reduction peak potential shifts to less negative overpotential values when pH < 2.[8,16,20]

A lesser amount than quinones, some researchers have studied the oxygen reduction reaction with azobenzene modified electrodes, as indicated in Table 2.

Sljukic *et al.*[21] studied the oxygen reduction reaction using glassy carbon electrodes or pyrolytic graphite modified with azobenzene and its derivatives. Cyclic voltammetry of an azobenzene-modified pyrolytic graphite electrode, recorded in phosphate buffer with pH = 2, showed a reduction peak at −0.6 V *vs.* ECS, which corresponds to the reduction of azobenzene to hydroazobenzene. The corresponding oxidation peak was observed at +0.4 V *vs.* ECS. The authors also found that when the potential was scanned more negatively, the reduction of hydroazobenzene to aniline at −1.2 V *vs.* ECS was irreversible.[21,27,28]

Cyclic voltammetry of an azobenzene-modified gold electrode showed a relation between redox peaks and scan rate.[22] At low scan rates, only one oxidation peak and one reduction peak were observed, involving 2 protons and 2 electrons in a single step, characterizing trans-azobenzene[29]. At high scan rates (≥ 300 mV s^{-1}), two reversible peaks were visible, corresponding to a two-step *cis*-azobenzene reaction, i.e., one proton and one electron in each step.[22]

Glassy carbon electrodes modified with azobenzene shifted the oxygen reduction reaction to less negative

Table 1. Quinone-modified electrodes used in oxygen reduction reactions

Catalyst	Modification	Solution, pH	Ref.
anthraquinone	Electrochemical reduction on glassy carbon (GC)	0.1 mol L^{-1} KOH	9-12
phenanthrenequinone	Electrochemical reduction on GC	0.1 mol L^{-1} KOH	13
9,10-phenanthraquinone	Adsorption on GC	Buffer (pH = 10)	8
1,2-naphthoquinone	Adsorption on GC	Phosphate buffer (pH = 7)	8
1,2-dyhidroxyanthraquinone (alizarin)	Adsorption on GC	Buffer (pH = 3)	14
1,4-naphthoquinone and its derivatives	Adsorption on carbon paste	Phosphate buffer (pH = 8)	15
naphthoquinone	Electrophoretic deposition on GC	Phosphate buffer (pH = 7)	16
polymeric 9,10-anthraquinone	Adsorption on GC	Buffers (pH = 2-9)	17
1,4-hydroxy-9,10-anthraquinone erivatives	Adsorption on GC	Buffers (pH = 1-13)	18
1,4-naphthoquinone	Adsorption on pyrolytic graphite	1.0 mol L^{-1} NaOH	19

Table 2. Azobenzene modified electrodes used in oxygen reduction reactions

Catalyst	Modification	Solution, pH	Ref.
Azobenzene and derivatives	Adsorption on GC; Adsorption on graphite	Phosphate buffer (pH = 2)	21
Azobenzene and derivatives	Self-assembled monolayers on gold (SAM)	Buffer B-R (pH = 5)	22-26

potential values (−0.37 V *vs.* ECS) compared with the noncatalyzed glassy carbon electrode (−0.53 V *vs.* ECS).[21] This indicates that azobenzene-modified electrodes have good electrocatalytic activity for H_2O_2 production.[21]

The incorporation of solid catalysts into the EDG graphitic mass is a novel application and the first results obtained by our group started to be reported last year. One of our papers[30] introduces the subject with the phrase: "Quinones have already proved their efficiency in the synthesis of hydrogen peroxide" and, although traditional they are still defeating our knowledge about how do they work and how to place them in the reaction ambient for obtaining the best catalytic effects and reaction rates.

Thus, the objective of the present work was to perform a comparative study among graphite pigment based gas diffusion electrodes (GDE) modified by 2-ethylanthraquinone, 2-*terc*-butylanthraquinone and azobenzene. These organic compounds were incorporated into the graphitic mass before the electrode pressing and their performance as a catalyst was compared by following the oxygen reduction currents and the yield during hydrogen peroxide synthesis.

Experimental

Electrode preparation

Precursor mass for the modified gas diffusion electrode (MGDE) was prepared from Degussa Printex 6L conductive carbon-black graphite pigment. A 60% polytetrafluoroethylene dispersion (Dyneon TF 5035 PTFE) was used as hydrophobic binder. The ratio of Printex to PTFE was 8/3.3, which is equivalent to 20% of PTFE. The mixture was homogenized in a 4:1 water:isopropanol bidistilled solution. The selected amounts of organic redox catalysts 2-ethylanthraquinone (EAQ), azobenzene (AZO) and 2-*terc*-butylanthraquinone (BAQ) from 3%, 5% and 10% (m/m), relative to the carbon pigment, were incorporated into the MGDE precursor mass, which was dried at 110 °C for 24 h. A 200 mesh AISI 304 stainless steel screen current collector was placed at the bottom of a 60 mm diameter pressing tool, which was then filled with 8 g of the precursor mass. Sintered 3 mm thick MGDE was obtained after 1.5 h at 310 °C, under a load of 18 MPa.

MGDE behavior

For voltammetric and electrolytic experiments, an electrochemical cell (one compartment, 250 mL) was used (Figure 1). GDE prepared with different concentrations of EAQ, BAQ and AZO (3, 5 and 10%) was used as cathode. The MGDE was placed at the bottom of the cell with an exposed area of 19 cm^2, and the electrode was oxygen-back-fed. The reference was Ag/AgCl (KCl sat.), and platinum foil was used as the counter electrode (A = 24 cm^2). The cell was thermostatted at 20 °C. The supporting electrolyte was 0.1 mol L^{-1} H_2SO_4 plus 0.1 mol L^{-1} K_2SO_4, pH = 1. Experiments were performed under mechanical stirring.

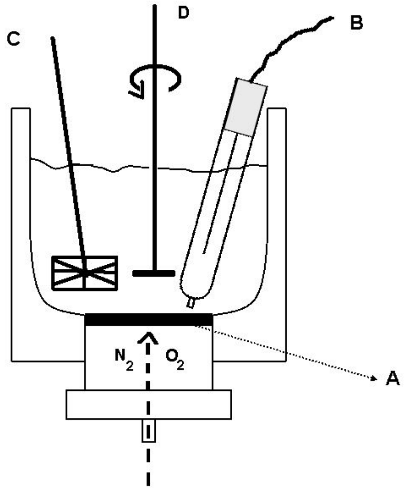

Figure 1. Scheme of the electrochemical cell used in the voltammetric and electrolytic experiments. (A) Working electrode (GDE or MGDE); (B) Reference electrode (Ag/AgCl, KCl sat.); (C) Counter electrode (platinum foil) and (D) Mechanical stirring. Volume of solution: 250 mL.

Linear voltammetry measurements were recorded from −0.2 V to −1.0 V *vs.* Ag/AgCl at 20 mV s^{-1}. The supporting electrolyte was previously saturated with nitrogen. Afterwards, i/E responses were also recorded in the presence of oxygen.

Subsequently, controlled potential electrolysis was employed to optimize the H_2O_2 electrogeneration rate relative to the applied potential in the range of $-0.4 \le E \le -0.9$ V *vs.* Ag/AgCl for MGDE, and $-0.6 \le E \le -1.0$ V *vs.* Ag/AgCl for GDE. During electrolysis an oxygen pressure of 0.16 bar was kept through the reverse side of the electrode. The electrolyte was sampled at 5 min intervals for the first half hour, and every 10 minutes thereafter. Electrolysis experiments were conducted in duplicate.

The hydrogen peroxide concentration was determined with a UV-Vis spectrophotometer (Lambda 40, Perkin Elmer Instruments), recording the spectra over 200 to 500 nm. A solution of 2.4 mmol L^{-1} $(NH_4)_6Mo_7O_{24}.4H_2O$ in 0.5 mol L^{-1} H_2SO_4 was added to the samples, resulting in a yellow color.[31] The absorbance was determined at 350 nm. Calibration plots based on Beer-Lambert's law were established relating absorbance to concentration.

To verify whether redox catalysts dissolve in the highly acidic medium used as supporting electrolyte (pH = 1), the solutions after electrolysis were analyzed by the High Performance Liquid Chromatography technique (Shimadzu, model 20A), using an SPD-20A UV/Visible detector, an automatic sampler, and a DGU-20A5 degasser coupled to a PC microcomputer. The stationary phase was a 250 x 4.6 mm Shimadzu Shim Pack CLC - ODS (M) column (column C18), and the mobile phase was acetonitrile (100%). The mobile phase flow rate was 1.0 mL min^{-1}, and wavelengths analyzed by the UV/Visible detector were 254 and 325 nm for quinones[32] and 365 nm for azobenzene.[33]

Results and Discussion

Voltammetric experiments

To study the electrochemical behavior of electrodes, linear voltammograms were recorded in the cathode region in a medium of 0.1 mol L^{-1} H_2SO_4 plus 0.1 mol L^{-1} K_2SO_4.

Figure 2 shows linear voltammetries (LV) recorded for electrodes with different concentrations of (A) 2-ethylanthraquinone, (B) 2-*terc*-butylanthraquinone and (C) azobenzene and a constant O_2 flow (P = 0.16 bar). Figure 3 compares the LVs recorded for MGDE (10%) under N_2 and O_2 flows. The (LV_{O2} - LV_{N2}) curves were obtained by subtracting LV current values recorded with O_2 from those recorded with N_2.

The curves in Figures 2 and 3 exhibit two current plateaus not well defined associated with the O_2 reduction reaction to H_2O_2 (reaction 3), and its subsequent reduction to water (reaction 4).

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \qquad (3)$$

$$H_2O_2 + 2\,H^+ + 2e^- \rightarrow 2\,H_2O \qquad (4)$$

The first plateau is observed between −0.3 and −0.7 V *vs.* Ag/AgCl (reaction 3), and the second step starting from −0.7 V *vs.* Ag/AgCl (reaction 4). Separation between the two steps of the oxygen reduction reaction is 400 mV, allowing these electrodes to be used in the production of hydrogen peroxide.

Regardless of the nature of the catalyst added to the GDE, higher current values were consistently observed; indicating that the oxygen reduction reaction on modified GDEs occurred at less negative overpotentials compared to a noncatalyzed GDE, indicating that GDE modification by organic redox catalysts improved the efficiency of hydrogen peroxide electrogeneration.

Current values increased with catalyst concentration in all three cases, probably as a result of two simultaneous processes: oxygen reduction on the graphite surface (electrochemical step), and the catalyst redox reaction that reduces O_2 (chemical step). When the catalyst concentration

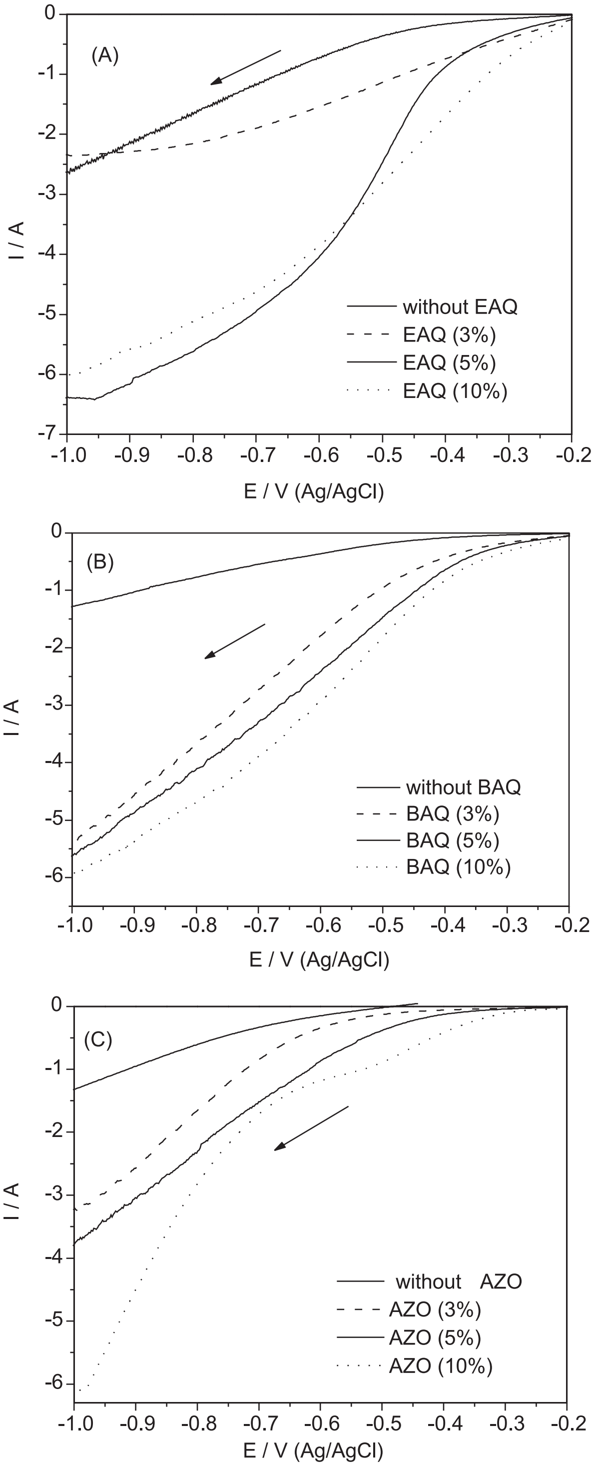

Figure 2. Linear voltammetry (LV) of GDEs modified by: (A) 2-ethylanthraquinone (EAQ); (B) 2-*terc*-butylanthraquinone (BAQ); and (C) azobenzene (AZO). Oxygen-purged supporting electrolyte, pressure of 0.16 Bar. Supporting electrolyte 0.1 mol L^{-1} H_2SO_4 plus 0.1 mol L^{-1} K_2SO_4, ν = 20 mV s^{-1}, T = 20 ºC, mechanical stirring.

is increased, the current also increases in response to the reduction in the overpotential required for the oxygen reduction reaction.

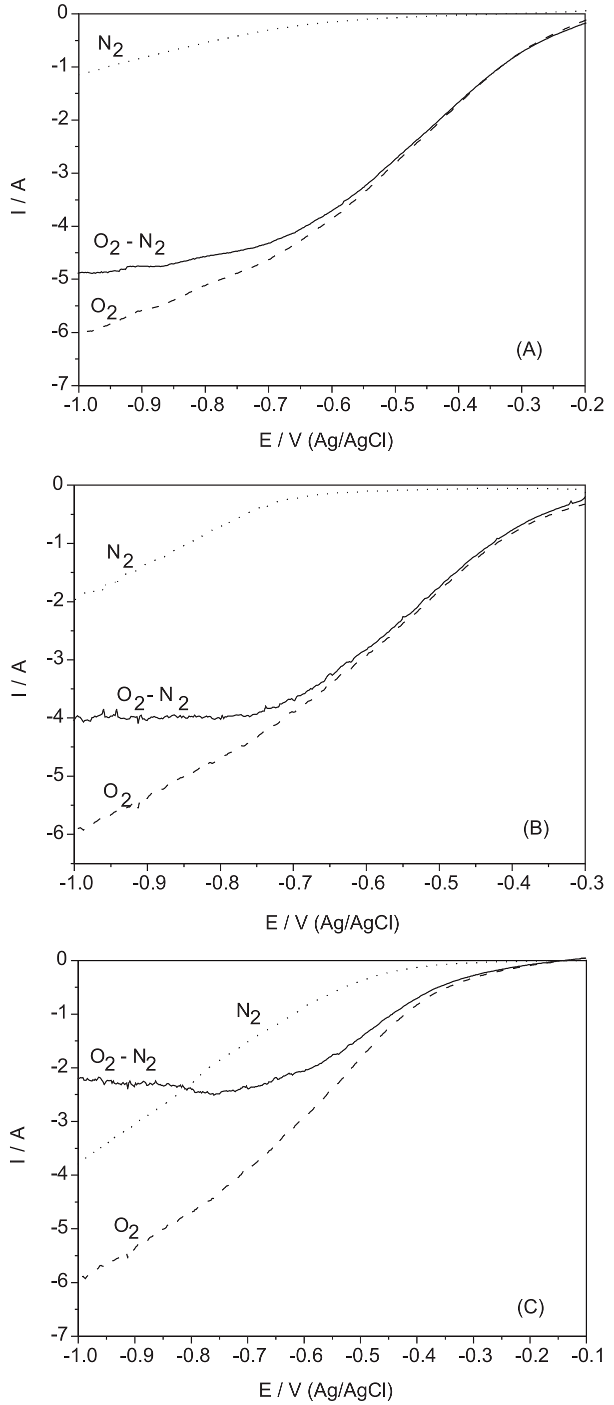

Figure 3. Linear voltammetry (LV) of GDEs modified by 10% of: (A) 2-ethylanthraquinone (EAQ); (B) 2-*terc*-butylanthraquinone (BAQ); and (C) azobenzene (AZO). Comparison of LVs recorded under N_2 and O_2 flows. The (LV_{O2} - LV_{N2}) curves were obtained by subtracting LV current values recorded with O_2 from those recorded with N_2. Flow with P = 0.16 bar, supporting electrolyte 0.1 mol L^{-1} H_2SO_4 plus 0.1 mol L^{-1} K_2SO_4, ν = 20 mV s^{-1}, T = 20 ºC, mechanical stirring.

Electrolysis at controlled potential

To monitor the hydrogen peroxide electrogeneration, electrolyses were performed at constant potential, and the contents were monitored by collecting samples at regular intervals and analyzing them by UV-Vis spectrophotometry.

The production H_2O_2 in function of time electrolysis for GDE modified by 10% of catalysts is show in the Figure 4. In every case, the electrogenerated H_2O_2 concentration increased linearly over time.

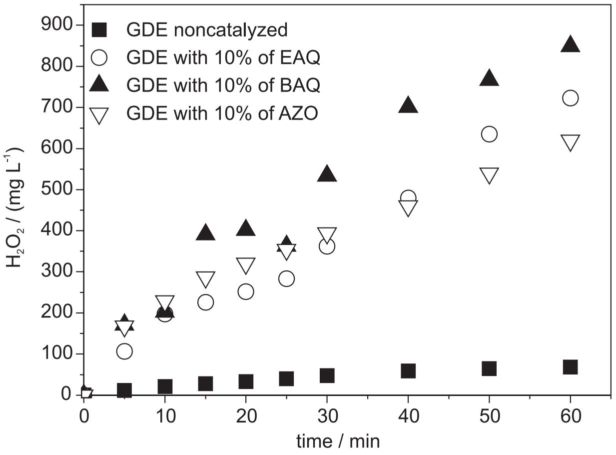

Figure 4. H_2O_2 production as function of electrolysis time for GDE modified by 10% of catalysts. Supporting electrolyte 0.1 mol L^{-1} H_2SO_4 plus 0.1 mol L^{-1} K_2SO_4, ν = 20 mV s^{-1}, T = 20 ºC, O_2 flow (P = 0.16 bar).

The Figures 5-7 show electrogenerated H_2O_2 content after one hour of electrolysis in function of the applied potential. H_2O_2 electrogeneration by noncatalyzed GDE increased with the applied potential, reaching its best yield at potential of –1.0 V *vs.* Ag/AgCl (567 mg L^{-1} of H_2O_2).

On the other hand, the results of electrolyses using GDEs modified with EAQ or BAQ (Figures 5 and 6) reached higher yields at the potential of –0.6 V *vs.* Ag/AgCl, when the electrogenerated H_2O_2 concentration reached its maximum. The behavior observed in the LVs experiments was confirmed, i.e., an initial increase up to –0.6 V *vs.* Ag/AgCl related with the oxygen reduction reaction (reaction 3), and from –0.7 V *vs.* Ag/AgCl the H_2O_2 the efficiency of the production process began to decline because of the decomposition of the electrogenerated hydrogen peroxide with the formation of H_2O *via* 4 electrons transfer (reaction 4).

Our results indicated that GDEs modified with EAQ or BAQ are more efficient than noncatalyzed GDE: in addition to increasing the H_2O_2 yield by about 30%, the H_2O_2 electrogeneration overpotential was reduced by 400 mV, reducing the consumption of energy.

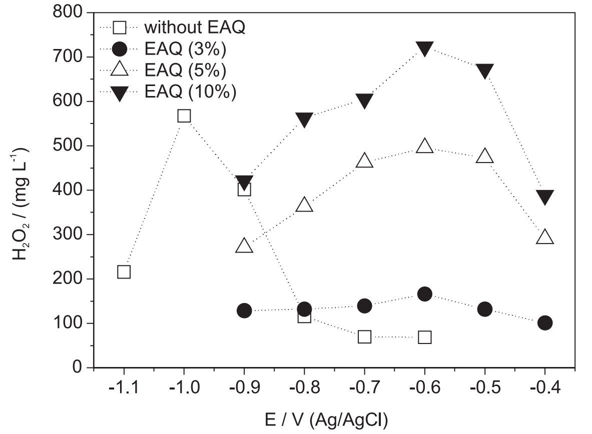

Figure 5. H_2O_2 production after 1 hour of electrolysis with EAQ, as function of applied potential. Supporting electrolyte 0.1 mol L^{-1} H_2SO_4 plus 0.1 mol L^{-1} K_2SO_4, ν = 20 mV s^{-1}, T = 20 ºC, O_2 flow (P = 0.16 bar).

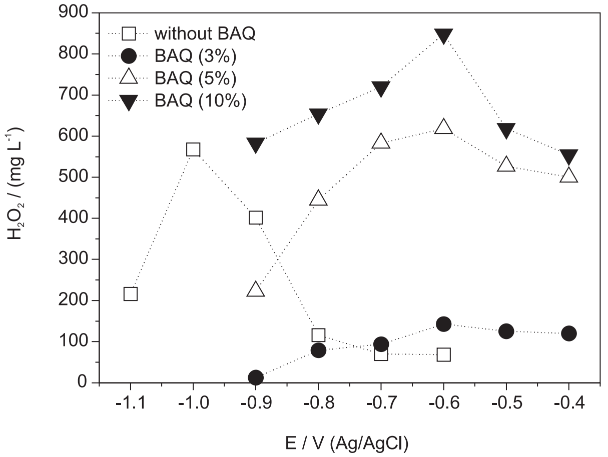

Figure 6. H_2O_2 production after 1 hour of electrolysis with BAQ, as function of applied potential. Supporting electrolyte 0.1 mol L^{-1} H_2SO_4 plus 0.1 mol L^{-1} K_2SO_4, ν = 20 mV s^{-1}, T = 20 ºC, O_2 flow (P = 0.16 bar).

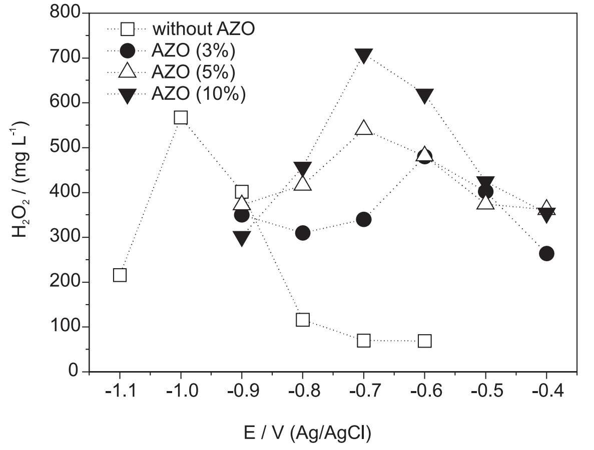

Figure 7. H_2O_2 production after 1 hour of electrolysis with AZO, as function of applied potential. Supporting electrolyte 0.1 mol L^{-1} H_2SO_4 plus 0.1 mol L^{-1} K_2SO_4, ν = 20 mV s^{-1}, T = 20 ºC, O_2 flow (P = 0.16 bar).

GDE modification with AZO also increased the catalytic activity for H_2O_2 electrogeneration (Figure 7) and a higher yield was observed compared with the noncatalyzed GDE. As for the applied potential, the maximum yield was obtained at –0.7 V *vs.* Ag/AgCl, displacing the overpotential for H_2O_2 generation by 300 mV to less negative values.

Comparison of the efficiency of catalysts added to GDE

Figure 8 shows a comparison of the electrogenerated H_2O_2 after 1 hour of electrolysis applying –0.6 V as function of the concentration of each catalyst used to modify GDEs. In general, GDE modification by redox organic catalysts resulted in more efficient H_2O_2 electrogeneration, with lower energy consumption compared to noncatalyzed GDE due to a lower overpotential of the oxygen reduction reaction. In every case, the production of H_2O_2 increased along with the catalyst concentration.

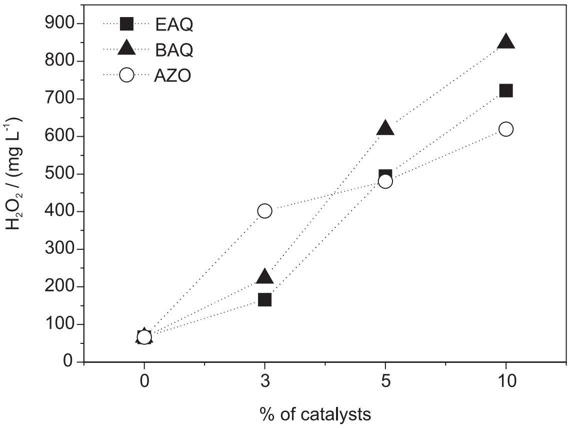

Figure 8. H_2O_2 electrogeneration after 1 hour of electrolysis at –0.6 V *vs.* Ag/AgCl as function of the concentration of each catalyst used as GDE modifier.

Comparing the results of H_2O_2 production as a function of the catalyst, under –0.6 V, BAQ was the most efficient for concentration higher than 5% reaching a yield of 850 mg L^{-1} of H_2O_2. However, modifying the GDE modification with just 3% AZO resulted in H_2O_2 contents equal to one half of that production volume.

An important electrochemical parameter is energy consumption (EC), which was computed from the cell potential monitored during electrolyses. Keeping the catalyst concentration at 10%, the values of energy consumption (kWh kg^{-1} of produced H_2O_2) were compared, as shown in Table 3.

Table 3 shows that the modification by quinones was more efficient than by azobenzene. In terms of electrogenerated H_2O_2 and required overpotential, GDE modification by BAQ was more efficient, but in terms of

Table 3. Comparison of energy consumption (EC) of each GDE studied for H_2O_2 production at −0.6 V *vs*. Ag/AgCl

Catalyst	H_2O_2 / (mg L^{-1})	Energy consumption / (kWh kg^{-1})
noncatalyzed	68.6	596.5
EAQ	722.8	232.4
BAQ	848.6	325.2
AZO	620.3	349.7

energy consumption, GDE modification by EAQ was more efficient. When the cost of catalysts is taken into account, the efficiency of EAQ modified GDEs is even higher: its modification costs 4-fold less than by BAQ. In conclusion, modification of GDEs by EAQ offers a better cost/benefit ratio than by other catalysts.

To check whether the catalysts dissolve in the highly acidic medium used as supporting electrolyte (pH = 1), analyses were done by High Performance Liquid Chromatography. These analyses involved standards of 2-ethylanthraquinone and azobenzene (both dissolved in acetonitrile to 140 ppm), the supporting electrolyte (0.1 mol L^{-1} H_2SO_4 plus 0.1 mol L^{-1} K_2SO_4) and samples collected at the end of electrolyses. Chromatograms showed peaks of EAQ standard solutions at 4.6 min, and of AZO at 4.7 min. No peaks associated with the catalysts were detected in the solution after electrolyses, and it was concluded that organic compounds added to the GDE do not dissolve in the supporting electrolyte (0.1 mol L^{-1} H_2SO_4 plus 0.1 mol L^{-1} K_2SO_4, pH = 1).

Conclusions

Our results indicated a great potential for the use of gas diffusion electrodes modified by organic redox catalysts 2-ethylanthraquinone, 2-*terc*-butylanthraquinone and azobenzene for *in situ* H_2O_2 electrogeneration. The results of constant potential electrolyses showed that H_2O_2 electrogeneration was efficient, and strongly dependent on the applied potential.

In addition to a considerable amount of H_2O_2 electrogenerated in acidic medium, these electrodes required less energy, as the H_2O_2 electrogeneration reaction overpotential shifted to less negative values compared to noncatalyzed GDEs. Our findings indicated that the best electrode for H_2O_2 electrogeneration is the GDE modified with 10% of 2-ethylanthraquinone, offering the best cost/benefit ratio.

Acknowledgments

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