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Comparative study of hydrogen peroxide electro-generation on gas-diffusion electrodes in undivided and membrane cells

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Abstract

The generation of hydrogen peroxide by means of the cathodic reduction of oxygen at gas-diffusion electrodes with a near 100% current efficiency was achieved in concentrations sufficient for the mineralization of refractory organics in Fenton treatment. A decrease in current efficiency over time at high temperatures and high current densities was observed. The polarization study carried out in potentiostatic, potentiodynamic and galvanostatic modes in 0.5 M Na_2SO_4 solution at pH 3 showed that the destruction of hydrogen peroxide at the cathode of the electrochemical reactor, as well as its chemical decomposition in the bulk solution, takes place at a significantly lower rate than the oxidation of H_2O_2 at the Ti–IrO_2 anode. Preparative electrolysis in the membrane reactor showed much higher current efficiencies for H_2O_2 electro-generation in comparison with tests carried out in an undivided cell. The performance of different proton-exchange membrane in this process was studied and a membrane cell with a heterogeneous MK-40 type PEM was found to be suitable. An optimized cell design, the appropriate selection of electrodes, supporting electrolytes, and a membrane resulted in a lower voltage in the membrane cell in comparison with the undivided cell.

1. Introduction

Hydrogen peroxide ($E^0_{pH0} = 1.78$ V) is a major reagent in Advanced Oxidation Processes (AOP) of wastewater treatment where a powerful oxidant, the hydroxyl radical ($E^0_{pH0} = 2.8$ V), capable of treating the most refractory organic pollutants is formed:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + ^{*}OH + OH^- \quad (1)$$

$$H_2O_2 \xrightarrow{h\nu} 2^{*}OH \quad (2)$$

$$O_3 + H_2O_2 \rightarrow 2^{*}OH + 3/2O_2 \quad (3)$$

Fenton [1] was the first to study the catalytic destruction of hydrogen peroxide by Fe^{2+} ions (reaction 1). In current practice this process is used in wastewater treatment. Ultraviolet radiation and ozone are also used in wastewater treatment and in the purification of potable water [2].

The generation of hydrogen peroxide solutions by means of the electrochemical reduction of oxygen at the cathode of an electrochemical cell proceeds with relatively low overpotentials

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad \text{(acid solutions)}, \quad E^o = 0.67V \quad (4)$$

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad \text{(alkaline solutions)}, \quad E^o = -0.065V \quad (5)$$

Due to the poor solubility of oxygen in aqueous solutions, three-dimensional electrodes of high specific surface area are needed to supply commercially reasonable current densities for the practical implementation of these processes. Different types of packed bed cells with carbon chips, felt, and reticulated vitreous carbon electrodes, have been used for H_2O_2 generation in alkaline solutions, mainly for utilization as a bleaching agent in the pulp and paper industry [3–7].

The electrogeneration of H_2O_2 is also used in organic electrosynthesis where the formation of hydroxyl radicals using the Fenton reaction leads to the conversion of aromatic hydro-carbons to phenols and/or aldehides; alkyl benzenes to alcohols; or aldehides and indoles to oxindoles [8]. It is also used in bioelectrosynthesis where more selective hydrogen peroxide oxidants (e.g. peroxidase enzymes) are needed [9]. Depolarisation of the cathodic reaction overpotential was also obtained in the electrosynthesis of other oxidants (for example potassium permanganate) where hydrogen evolution was replaced either by reduction of oxygen on porous nickel cathodes, or by means of bubbling of air through the bipolar packed bed of ferro-manganese particles [10–12].

Gas-diffusion electrodes (GDE) with a catalytically active hydrophilic layer on one side of the carbon cloth matrix facing the solution and its PTFE impregnated hydrophobic reverse side used for oxygen supply to the 3-phase interface for the hydrogen peroxide electrosynthesis has been studied [13–18] but the data for cell voltage and the specific energy consumption for H_2O_2 electro-generation are not available in these reports. Along with the fact that the relatively high concentration (7.1 kg m^{-3} Na_2SO_4) of supporting electrolytes used in these studies is not typical for wastewater, this lack of information is the reason why estimation of the economic efficiency of GDE application in industrial wastewater treatment based on these references is difficult.

The present research was carried out: (1) To optimize cell design using different undivided and membrane reactors, (2) To determine the influence of the process parameters: electrolyte temperature and pH composition and concentrations of the supporting electrolyte and the means of oxygen and air supply to the GDE on H_2O_2 current efficiency and specific energy consumption.

2. Experimental

2.1. *Chemicals and analytical procedures*

All solutions were prepared with distilled water and with chemical grade reagents. Sulfuric acid and concentrated H_2O_2 solutions were supplied by PFP (Japan) and sodium chloride, sodium sulfate and sodium hydroxide by Jin Chemical Pharm. Co. Ltd (S. Korea). pH was measured usingan ORION 420A+ pH meter. Hydrogen peroxide concentration was measured through a standard titration method using potassium permanganate [19].

2.2. *Electrochemical reactors and electrodes*

Potentiostatic, potentiodynamic and galvanostatic tests were carried out in a standard 3-electrode glass cell. A GDE with a 0.33 cm^2 surface area acted as a working electrode fixed in a teflon tube so that oxygen gas was supplied to the reverse side of the cathode. A saturated Ag/AgCl electrode was used as a reference and Pt mesh as auxiliary electrode.

Pilot tests of the hydrogen peroxide electro-generation process were carried out in a filter-press type Electro-MP cell. Initial trials (Table 1) were performed under conditions similar to those described in [17], with batch recirculation at a 360 l h^{-1} flow rate of 5 liters (in contrast with the 25 l volume in the cited work) of 0.05 M Na_2SO_4 solution in an undivided cell. An interelectrode gap of 6.5 mm was formed by plastic spacers (5 mm) and gaskets fixed between parallel electrodes with 100 cm^2 visible surface area (10 × 10 cm) each.

A DSA electrode designed for oxygen evolution was used as anode and a gas-diffusion electrode with a PTFE-impregnated carbon sheet coated with Black Pearls 2000 carbon black was used as cathode. The GDE was hot-pressed on a nickel mesh which acted as a current feeder to the graphite frame. The other tests were performed with a GDE sheet fixed mechanically between the spacer and the current feeder, either a perforated graphite plate or an Inconel mesh, welded to the frame of the same material (all supplied by Electrocell AB, Sweden). Oxygen was fed from the cylinder at a pressure of 0.01 MPa and a rate of 30 g h^{-1} to a gas chamber placed after the cathode. Some tests were carried out with air instead of pure oxygen. Before the reaction, the air was passed through a silica gel bed for drying.

Cell design was partially changed in further tests (see section 3.1, Table 2). The set-up and components of such a cell with a substantially smaller inter-electrode gap in comparison with the original Electro-MP cell, is shown in Figure 1 We used spacers (3) of 3 mm width, mesh – type Ti–IrO_2 CSA anodes (5), and titanium mesh current feeders to the cathode welded on the titanium frame by means of side ribs all from TECHWIN Co.Ltd [20–22].

The 1 M H_2SO_4, pH 1.5 anolyte was continuously recycled from a special tank through an inlet tube in the plastic plate and a spacer (3) to the reverse side of the mesh anode (5). The cation-exchange membrane (6) was fixed between a mesh anode (5) and a spacer (7) with no gap. The GDE (8) was fixed between a titanium mesh current distributor (9) and a spacer (7) used for catholyte flow. As a result the interelectrode space was narrowed to one 3 mm spacer (7) width. Also, oxygen gas was supplied to the back side of the gas-diffusion cathode through the spacer (11) which served as a gas chamber. The on-site generation of O_2 of 95% purity for the GDE supply was obtained by using a WH-7 type Pressure Swing Adsorption (PSA) oxygen generator, produced by Won Hi Tech. Corp. DC power was taken from a HS-SCP type rectifier (Hyun Sung Co.).

3. Results and discussion

3.1. *Tests in undivided electrochemical reactors*

Table 1 shows changes in current efficiency, cell voltage and corresponding power consumption over time when 5 l of 0.05 M $Na_2SO_4 + H_2SO_4$ solution was treated at different pH values in an undivided cell with a 6.5 mm gap (5 mm on plastic spacers and 1.5 mm on rubber gaskets) and when pure oxygen was supplied to the GDE from the cylinder.

The effect of pH is illustrated in Figure 2(a). All tests were carried out at 5A (0.05 A cm^{-2}) and 25 °C. In acid and neutral solutions current efficiency decreased from 100 to 74–79% in the first 5 min; in 1 hit was only 2.67% for the same time at pH 13. The CE decrease in this case was even higher than that observed in a 1 M NaOH solution (from 100 to 12.05%, Figure 2(b)).

The pH value increased slightly in 1 h tests from 3.0 to 3.3. In contrast, pH decreased in tests at initial pH 6.5. This was even more notable in alkaline solutions where a decrease from pH 13 to pH 11.8 was observed.

Intensive H_2O_2 destruction at higher temperatures and current densities and in high alkaline solutions is evident from these test results. Specific energy consumption is minimal at lower pH and temperature in spite of a voltage decrease with temperature rise. It should be noted that at 5 A and 10 A the specific energy consumption at 25 °C and at 40 °C is the same.

Taking into account the price of pure oxygen, the next tests were carried out using compressed air fed to the GDE. The voltage changed slightly, but current efficiency was somewhat lower and specific energy consumption higher than in tests which used pure O_2 (Figure 3). It is clear however that, if necessary, the GDE can be supplied with air instead of oxygen without bringing about any essential changes in the process parameters.

After a number of tests the GDE was partially damaged because of the high values of air and/or water pressure increase in the cell. The penetration of acid solution through the carbon cloth affected the nickel mesh being used as a current feeder. Products of nickel corrosion covered the active surface of the GDE and decreased the efficiency of the electrode. A reversal of polarity caused a recovery of the current efficiency up to 75–80% from the initial level.

At least 0.5–1 g l^{-1} of H_2O_2 is usually needed to achieve the appropriate stoichiometry for a chemical Fenton reaction (1) of ferrous salt with H_2O_2 and organic pollutants present in wastewater (as well as for treatment with ozone or ultraviolet irradiation in other AOPs). However 1 g l^{-1} of hydrogen peroxide was not reached even after 1 h electrolysis when a 5-litre polluted solution was treated in an undivided cell at 5 A.

In tests with 10 A current, 20–21 kWh kg^{-1} was consumed in reaching a 0.5 g l^{-1} H_2O_2 solution. In Korea this corresponds to USD 1–1.1 to get 1 kg of 100% H_2O_2. This sum at least doubles when taking into account the price of 7.1 kg m $^{-3}$ sodium sulfate salt and the pure oxygen used in these tests, along with additional investment costs. This makes the price of creating electrogenerated H_2O_2 under the conditions suggested in [17] non-competitive with the commercial price of a hydrogen peroxide chemical produced by means of the anthraquinone process which is approximately USD 1.5 per kg H_2O_2 (100%).

Thus the following experimental conditions were changed. The concentration of Na_2SO_4 was lowered to 1 g l^{-1} which is close to the typical quantity of salts

Table 1. Data for hydrogen peroxide electro-generation test results for trials performed in a 6.5 mm gap (5 mm spacer + gaskets) undivided Electro- MP cell with pure oxygen supply to the GDE, treating 5 l of solution: 0.05 M Na_2SO_4, pH: 3; 6,5; 10 and 13; temperatures: 25 °C; 40 °C and 60 °C

Temperature/°C			25 °C			40 °C			60 °C		
PH	Current/A	Time/min	Voltage/V	C_{H2O2}/g l^{-1}	CE / %	Voltage / V	C_{H2O2}/ g L^{-1}	CE/%	Voltage/V	C_{H2O2}/g L^{-1}	CE/%
3	5	5	7.15	0.052	100.0	6.9	0.052	100.0	5.15	0.051	96.90
		30	7.22	0.272	85.75	6.5	0.255	80.00	5.19	0.149	46.91
		60	7.20	0.468	73.77	6.4	0.432	68.00	5.12	0.170	26.79
	10	5	12.3	0.105	100.0	12.0	0.105	100.0	8.51	0.102	96.59
		30	11.8	0.490	77.23	11.2	0.527	83.10	8.60	0.238	37.51
		60	12.1	0.854	67.30	11.2	0.816	64.35	8.60	0.238	18.76
	20	5	21.1	0.220	100.0	19.4	0.204	96.50	14.5	0.170	80.41
		30	21.1	0.986	77.72	17.7	0.782	61.67	14.7	0.416	32.83
		60	20,8	1.700	67.00	18.8	1.037	40.89	14.7	0.340	13.40
6.5	5	5	7.40	0.0527	100.0	5.8	0.052	100.0	5.1	0.0425	80.50
		30	7.07	0.2720	85.75	5.8	0.238	75.03	5.1	0.1402	44.20
		60	6.95	0.5020	79.05	5.8	0.391	61.63	5.2	0.2040	32.16
	10	5	13.2	0.1056	100.0	10.6	0.105	100.0	8.4	0.0595	56.20
		30	12.6	0.5270	83.07	10.2	0.442	69.67	8.4	0.2380	37.50
		60	12.7	0.9440	74.37	10.4	0.748	58.96	8.6	0.3740	29.48
	20	5	21.6	0.1960	92.47	17.1	0.187	88.46	14.6	0.1450	68.35
		30	21.2	0.9100	71.69	17.1	0.740	58.29	14.6	0.5610	44.22
		60	21.6	1.6240	63.40	17.7	1.260	49.58	15.0	0.8610	32.16
10	5	5	7.8	0.0512	96.59						
		30	7.6	0.2290	72.35						
		60	7.54	0.3740	58.95						
13	5	5	3.96	0.0425	80.49						
		30	4.05	0.0255	8.03						
		60	4.00	0.0170	2.67						

Table 2. Hydrogen peroxide electro-generation in a 1 g l^{-1} $Na_2SO_4 + H_2SO_4$ solution at pH3, 25 °C in an undivided cell with 3 mm gap at 0.05 A cm^{-2} and 0.07 A cm^{-2}

Current /A	5				7			
Time/min	Voltage/V	C_{H2O2}/g l^{-1}	CE/%	kWh kg^{-1}	Voltage/V	C_{H2O2}/g l^{-1}	CE/%	KWh kg^{-1}
5	7.82	0.265	100	12.3	10.39	0.37	100	16.38
10	7.77	0.474	88.25	13.9	10.27	0.677	91.43	17.69
15	7.69	0.663	84.89	14.3	10.05	0.956	86.12	18.39
20	7.59	0.854	80.48	14.9	9.90	1.216	82.14	18.99
25	7.51	0.999	76.37	15.5	9.79	1.456	78.7	19.61
30	7.45	1.153	73.78	15.9	9.62	1.684	75.85	19.99
35	7.44	1.270	70.77	16.6	9.61	1.866	72.07	21.02
40	7.37	1.392	68.13	17.06	9.52	2.044	69.05	21.73
45	7.36	1.514	66.15	17.5	9.44	2.203	66.16	22.49
50	7.32	1.599	63.88	18.07	9.41	2.354	63.62	23.31
55	7.29	1.671	61.55	18.67	9.27	2.477	60.87	24.01
60	7.28	1.770	59.45	19.3	9.25	2.593	58.39	24.97

found in industrial and municipal wastewaters. The inter-electrode gap was narrowed when mesh-type electrodes were welded to the frame by side ribs (as shown in Figure 1), which excludes the thickness of gaskets in this package. Thinner (3 mm) spacers of an improved design ensured a uniform solution flow between electrodes. The solution volume was decreased 5 times to 1 liter to minimize the time necessary to achieve the same concentration of H_2O_2 in a cell where the hydrogen peroxide destruction rate is very high. 25 l of the same solution was treated with the same current in study [17] and current efficiency was much lower.

A titanium mesh with an outer size of 10 × 10 cm, coated with IrO_2 (TECHWIN Co. ltd. [20–23]), was used as anode. Either perforated graphite plates or Inconel mesh (which are more stable than nickel in acid solutions) were used as current feeders to the GDE. Furthermore, oxygen to the GDE was supplied not from a cylinder but from a PSA generator which produces O_2 of 90–95% purity. The results of 1 liter of 1 g l^{1} Na_2SO_4 + H_2SO_4 solution treatment during 1 h in such cells are summarized in Table 2 and are much better than those in Table 1.

As in the previous case, better results were obtained at pH 3 in comparison with neutral and alkaline solutions (see Figure 4(a, b)) but though a current efficiency decrease was also observed in these tests, the rate of H_2O_2 decomposition was lower and much higher concentrations of hydrogen peroxide were obtained with less power consumption.

For example, a 1 g l^{-1} H_2O_2 solution was generated at 5 A after 25 min with 15.5 kWh kg^{-1} of power consumption which corresponds to USD 0.85 per kg of H_2O_2. The price of 1 g l^{-1} Na_2SO_4 added as a supporting electrolyte is negligible, taking into account that in practice industrial wastewater usually contains significant amounts of salts with the same conductivity making the addition of salt unnecessary.

At the same time, when a PSA generator is used the price of oxygen supply is reduced to the price of power for the air compressor. Therefore, based on these results, we can conclude that the on-site electrochemical generation of hydrogen peroxide solutions – even in undivided cells – can be quite cost-competitive for wastewater treatment. The safety of on-site generated dilute solutions of hydrogen peroxide gives additional

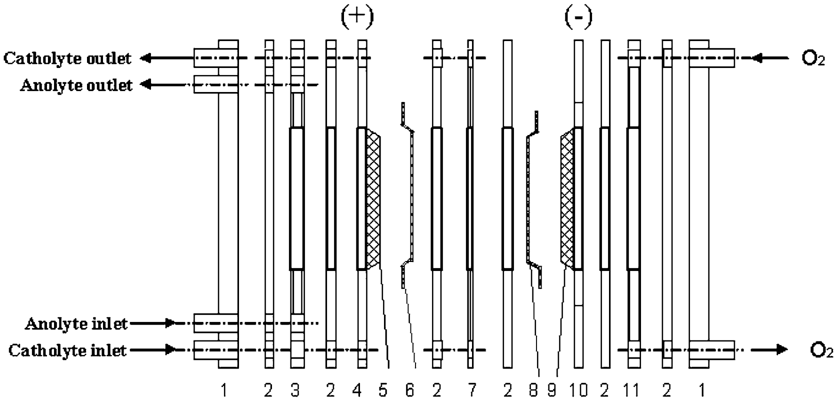

Fig. 1. Set-up and components of the electrochemical cell. Legend: (1) Plastic plates with manifolds for electrolyte and gas inlet and outlet, (2) rubber gaskets, (3) Plastic frame with spacer for electrolyte flow, (4) Titanium frame as a current feeder, (5) Ti–IrO_2–SnO_2 catalytic stable anode mesh, (6) Proton-exchange membrane, (7) Gas-diffusion electrode, (8) Titanium mesh as a cathode current distributor, (9) Titanium frame as a current feeder, (10) Plastic frame as a gas chamber. Stainless steel end plates and through holes for coupling bolts are not shown.

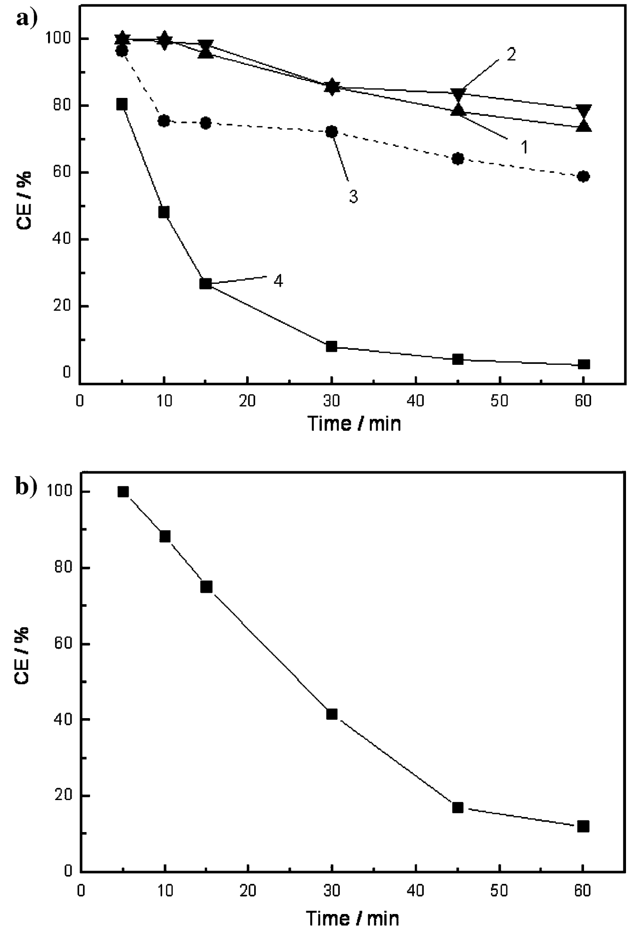

Fig. 2. Effect of solution pH on H_2O_2 generation current efficiency – time relation for 0.05 M Na_2SO_4 solution treatment in the undivided cell at 0.05 A cm^{-2}, 25 °C and pH: (a) 1–3; 2–6.5; 3–10; 4–13; (b) in 1 M NaOH.

advantages if we consider the problems of transportation and concentrated solution storage.

3.2. *Study of the H_2O_2 destruction processes*

The time decrease in current efficiency, observed in all tests in an undivided cell is attributable to different modes of hydrogen peroxide decomposition:

1. Oxidation at the anode :

$$H_2O_2 \quad \rightarrow O_2 + 2H^+ + 2e^- \tag{6}$$

2. Reduction at the cathode :

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{7}$$

3. Chemical decomposition in the balk of solution:

$$2H_2O_2 \rightarrow O_2 + 2H_2O \tag{8}$$

4. Interaction with active chlorine formed when chloride-ions are present in the solution:

$$H_2O_2 + NaOCl \rightarrow NaCl + O_2 + H_2O \tag{9}$$

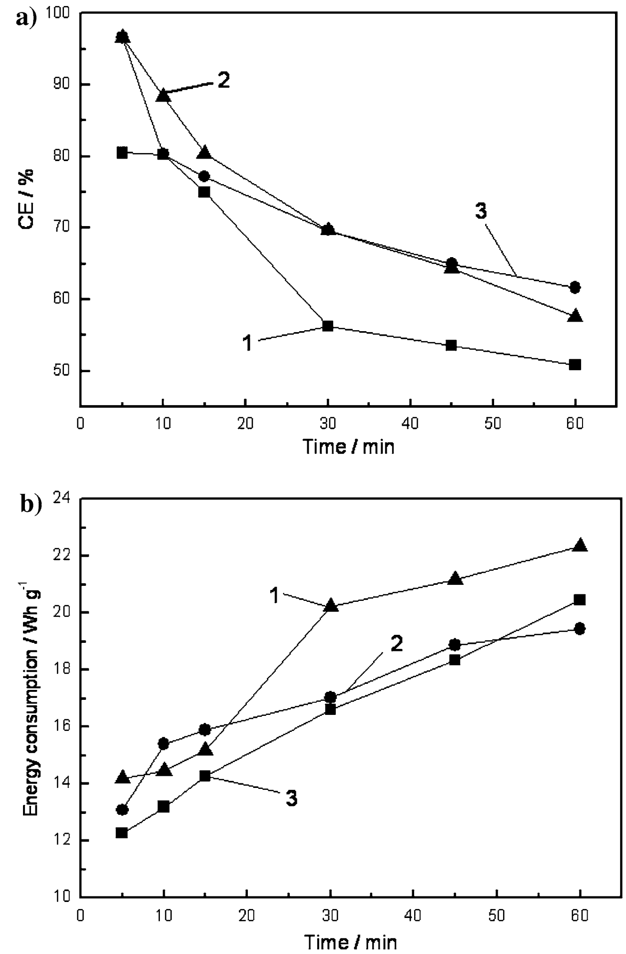

Fig. 3. Variation of current efficiency (a) and specific energy consumption (b) of H_2O_2 generation with time with different air pressures supplied to the GDE, MPa: 1–0.01; 2–0.015; 3–0.02; Solution: 0.05 M $Na_2SO_4 + H_2SO_4$, pH 3; temperature 25 °C; 0.05 A cm^{-2}; (Undivided cell).

5. Reactions with intermediate products of oxygen reduction at the cathode (O_2^-, *OH or *HO_2) [23, 24]:

$$O_2^- + H_2O_2 \rightarrow OH^- + O_2 + {}^*OH \tag{10}$$

$${}^*HO_2 + H_2O_2 \rightarrow O_2 + H_2O + {}^*OH \tag{11}$$

$${}^*OH + H_2O_2 \rightarrow {}^*HO_2 + H_2O \tag{12}$$

The rate of hydrogen peroxide destruction at the anode was studied on the basis of galvanostatic polarization curves detected in a 3-electrode glass cell with a titanium anode coated with a catalytic active layer of IrO_2.

The oxidation of water with oxygen evolution starts at 0.9 V vs Ag/AgCl (Figure 5, curve 1) in 0.5 M Na_2SO_4 supporting electrolyte at pH 3 in the absence of hydrogen peroxide. The anodic current increases by two orders in the case of a 0.34 g l^{-1} H_2O_2 addition (Figure 5, curve 2) which can be explained only by the

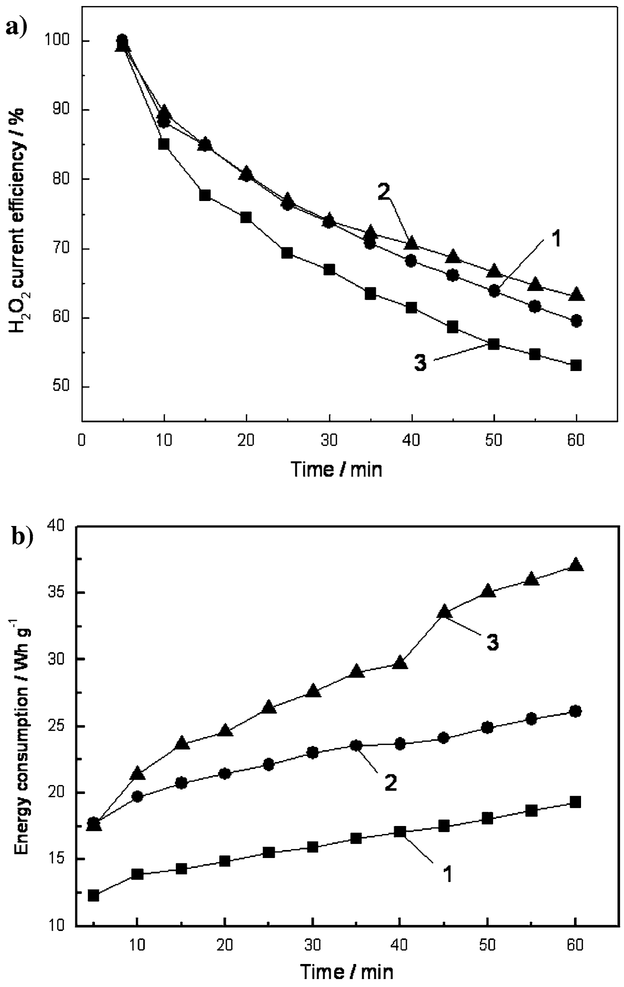

Fig. 4. Influence of solution pH on H_2O_2 generation current efficiency (a) and specific energy consumption (b) variation with time. Undivided cell at 0.05 A cm^{-2} with 0.5 l min^{-1} flow rate of 1 g l^{-1} Na_2SO_4 solution at 25 °C and different pH values : (1–3; 2–7; 3–12).

active oxidation of hydrogen peroxide at the anode (reaction 6). The shift of the polarization curve to less positive potentials was observed when the initial concentration of hydrogen peroxide was 8 g l^{-1} and 16 g l^{-1} (Figure 5, curves 3 and 4 respectively).

The effect of H_2O_2 concentration on the anodic destruction rate is shown in Figure 6, along with data from the preparative electrolysis performed at 3 A in the cell where compartments with a Ti-IrO_2 anode and a graphite plate cathode (100 cm^2 surface area each) were divided by a MK-40 type cation-exchange membrane. Solutions containing 1 g l^{-1} Na_2SO_4 + H_2SO_4 with different initial concentrations of H_2O_2 in the anolyte were treated at 25 °C and pH 3.

A final concentration of 0.108 g l^{-1} was obtained after 1 h of electrolysis in a solution with an initial concentration of 0.272 g l^{-1} (Figure 6, curve 1). So, 60.3% of the initial amount of hydrogen peroxide was destroyed which corresponds to 8.63% faradaic efficiency of the anodic current. Relatively less decay (from 1.224 to 0.89 g l^{-1}), which corresponds to 27.28% decay of the initial amount (or 17.57% efficiency) was observed in solutions with higher initial concentrations of H_2O_2.

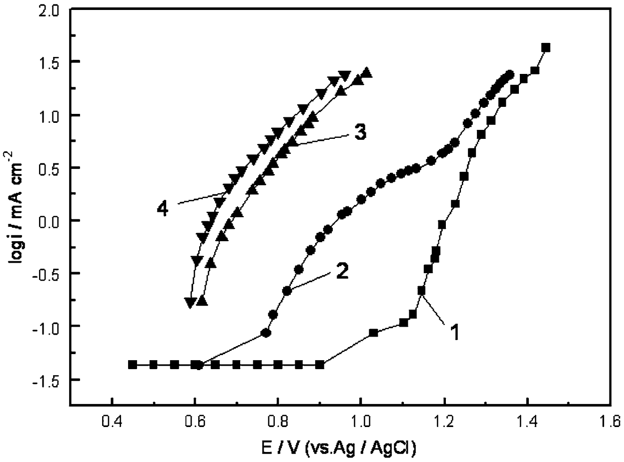

Fig. 5. Anodic galvanostatic curves of the Ti–IrO_2 CSA with a 0.23 cm^2 surface area on 25 °C in 0.5 M $Na_2SO_4 + H_2SO_4$ solution, pH 3 with H_2O_2 content, g l^{-1}: 0–(curve1); 0.34–(2); 8–(3); 16–(4).

The chemical decomposition of hydrogen peroxide in bulk solution is a slow process and significant losses of product during the 1 h electrolysis cannot be explained by reaction (8).

In order to study hydrogen peroxide destruction at the cathode (eq. 8) potentiodynamic polarization curves (Figure 7) were registered in 0.5 M $Na_2SO_4 + H_2SO_4$ supporting electrolyte at pH 3.

Three regions can be clearly distinguished in the voltammograms. The first wave with the limiting current at the potential −1 V (vs. Ag/AgCl) corresponds to O_2 reduction with H_2O_2 generation. Reaction (4) was proved by analysis of the product in the solution. Control tests with hydrogen peroxide addition were carried out to identify the nature of the second wave, by limiting the current at potentials of −1.8 to −2.0 V) but

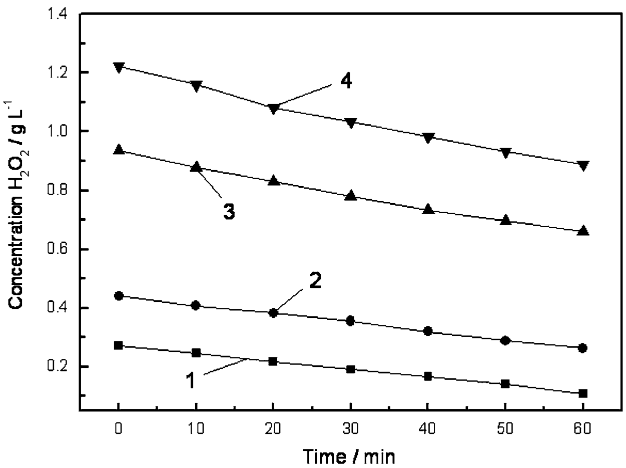

Fig. 6. Decay of hydrogen peroxide concentration over time, g l^{-1}: 1–0.272; 2–0.442; 3–0.935; 4–1.224) in 1 h tests, carried at a 3 A current in the membrane cell. Solution: 1 g l^{-1} $Na_2SO_4 + H_2SO_4$, pH 3, and 25 °C.

no changes of reaction rate were obtained. This means that the second wave cannot be attributed to cathodic reduction of H_2O_2 (reaction 7). In these tests hydrogen gas evolution was visually observed at potentials exceeding −2.3 V.

It should be mentioned in conclusion that the destruction of hydrogen peroxide at the cathode of the electrochemical reactor, as well as its chemical decomposition in the bulk solution, proceeds at a significantly lower rate than the anodic oxidation of H_2O_2. Thus hydrogen peroxide transport to the anode must be prevented.

3.3. *Hydrogen peroxide electro-generation in the membrane cell*

Cation-exchange membranes (CEM) prevent transportation of H_2O_2 to the anode and provide the transport of protons liberated at the anode chamber according to the reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{13}$$

to the cathode chamber. Therefore, the next series of tests was performed in a cell separated by a CEM.

The treatment of dilute solutions usually proceeds at higher voltages in membrane cells due to the wider inter-electrode space when compared to undivided electrochemical reactors. In the present work this problem was solved by the introduction of an improved cell design (Figure 1) where the acidic anolyte flowed at the back side of the anode mesh, to provide a minimal ohmic drop in the anolyte. Special spacers of 3 mm thickness were designed to get a uniform flow of catholyte in the inter-electrode space.

The membranes tested were Nafion 117 (Du Pont, USA), K-101 and K-171 (Asahi Glass, Japan), and MK-40 type Russian membranes. The latter were used because of their comparatively low price. Most modern homogeneous membranes are specially designed for the selective transport of Na^+ ions to the catholyte, which is very important in other industrial processes (e.g. Cl_2-NaOH production).

It is solely the proton transport which is needed in wastewater treatment processes, whereas the transport of Na^+ instead of H^+ ions leads to the formation of alkaline conditions in the cathode chamber which is followed by a very high rate of H_2O_2 decomposition. So the heterogeneous MK-40 membrane which is less selective to the transport of sodium ions looks preferable.

This is illustrated by the results at 5 A in the membrane cell separated by the MK-40 (Figure 8, curve 1) and Nafion 117 (Figure 8, curve 2) cation-exchange membranes, with 1 g l^{-1} $Na_2SO_4 + H_2SO_4$ as a catholyte at pH 3 and 100 g l^{-1} H_2SO_4 as an anolyte.

Sodium chloride, which is cheaper and has better electrical conduction than sodium sulfate, can be used as supporting electrolyte in the catholyte when CEM prevents the transport of Cl^--ions to the anode. That is one more advantage of the membrane cell which cannot be achieved in undivided reactors, because the active chlorine generated from chloride-ions interacts with hydrogen peroxide and thus lowers the oxidizing power of both oxidants (NaOCl and H_2O_2) according to reaction (9).

The results of tests, when 1 g l^{-1} $Na_2SO_4 + H_2SO_4$, pH 3 solution was treated at 3 A, 5 A and 7 A in a membrane cell with MK-40 PEM are shown in Figure 9, (a, b). Higher results were obtained at 3 A where the current efficiency was within 98–100 % in 35 min, and 1 g of H_2O_2 was generated in 1000 ml of treated solution with 7.45 kWh kg^{-1} specific energy consumption. The results at 5 A and 7 A loads in which 1 g l^{-1} H_2O_2 concentration was achieved in 25 min and 15 min,

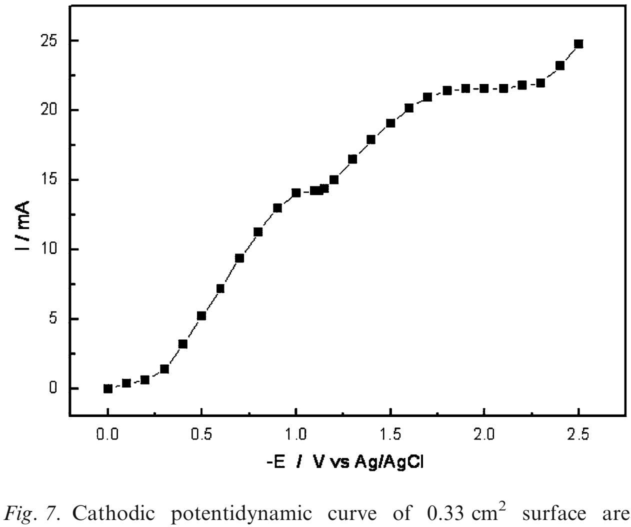

Fig. 7. Cathodic potentidynamic curve of 0.33 cm^2 surface area GDE polarization with 5 mV s^{-1} scan rate in 0.5 M $Na_2SO_4 + H_2SO_4$ solution, at pH 3 and 25 °C.

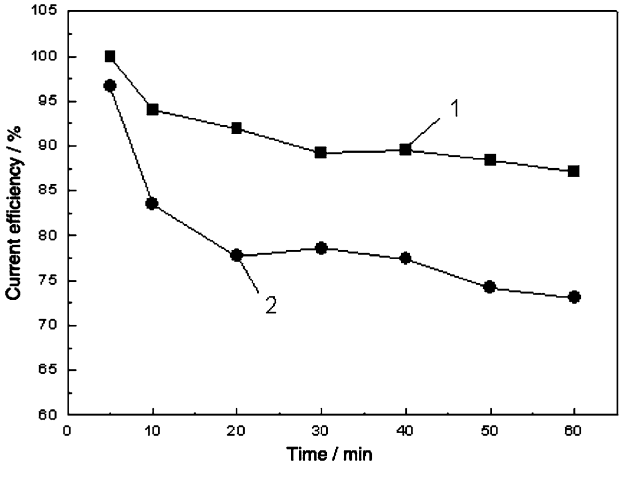

Fig. 8. H_2O_2 electro-generation current efficiency–electrolysis time dependence in tests, performed in reactor separated with MK-40 (1) and Nafion 117 (2) cation-exchange membranes at 25 °C. Solution −1 g l^{-1} $Na_2SO_4 + H_2SO_4$, pH 3.

respectively, with 11 kWh per kg_{H2O2} and 14 kWh per kg_{H2O2} specific power consumption are of great interest.

A comparison with results of tests carried out in an undivided cell with 7.1 g L^{-1} Na_2SO_4, as a supporting electrolyte (see Table 1), where 15.5 and 18.5 kWh per kg of H_2O_2 were consumed at the same current loads respectively, shows that a significant (25–30%) saving in energy consumption was achieved when the membrane cell was used. An even greater economy was achieved when 1 g l^{-1} sodium chloride was used instead of Na_2SO_4 as supporting electrolyte (Figure 10, curve 1). In contrast to the tests performed in an undivided cell, no pH change was observed in the catholyte of the membrane cell.

Comparison of these results with the data of tests (Figure 10, curve 2,3) in which different volumes (1 l and 25 l respectively) of 7.1 g l^{-1} $Na_2SO_4+H_2SO_4$ solution were used as supporting electrolyte, shows that along with an economy of salt use which is used in lower concentrations and is cheaper in the case of 1 g l^{-1} sodium chloride, current efficiency was significantly higher when a membrane cell was used. The average voltage for the membrane cell was 5.85 V and the specific energy consumption was 11.83 kWh per kg of H_2O_2.

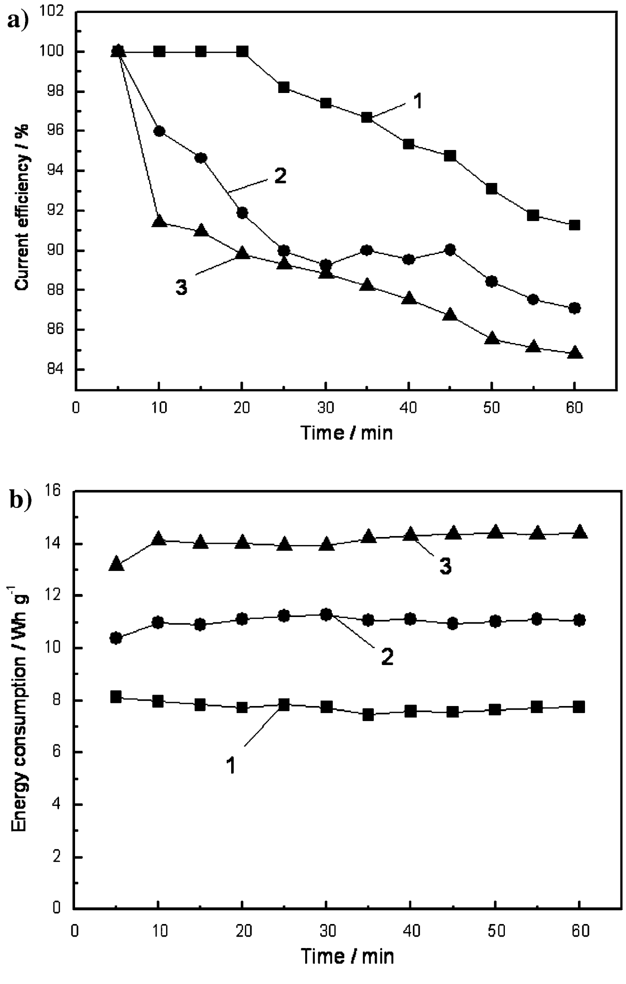

Fig. 9. Effect of current density variation, A cm^{-2}: (1–0.03; 2–0.05; 3–0.07) on H_2O_2 generation current efficiency (a) and specific energy consumption (b) over time. 1 litre of 1 g l^{-1} $Na_2SO_4+H_2SO_4$, pH 3 solution treatment in the membrane cell. Anolyte –1 M H_2SO_4.

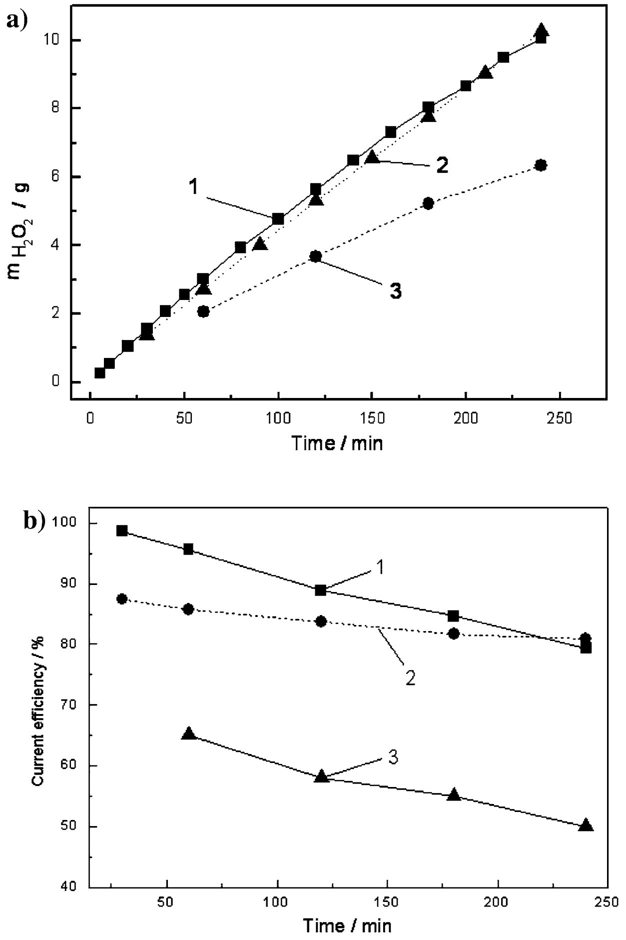

Fig. 10. Hydrogen peroxide accumulation (a) and variation of the current efficiency (b) with time in tests, carried out with recirculation of 1 l volume (curve 1) and 25 l volume (curve 2) of 1 g l^{-1} NaCl, pH 3 solution in the catholyte of the membrane cell in comparison with literature data of 25 l of 7.1 g l^{-1} (0.05 M) $Na_2SO_4+H_2SO_4$, pH 3 solution treatment in the undivided cell [17] at 0.05 A cm^{-2} applied current density (curve 3).

4. Conclusions

A systematic study of hydrogen peroxide electro-generation at a GDE in different supporting electrolytes was carried out at different current densities, temperatures and solution pH. In all cases a current efficiency reduction at high temperature (60 °C) and high current density (0.2 A cm^{-2}) was observed, especially in highly alkaline solutions.

Almost 100% current efficiency was achieved with the generation of 0.5–1 g l^{-1} hydrogen peroxide which is usually sufficient for the mineralization of organic pollutants in consecutive Fenton reactions. Results obtained in the cell divided by a proton-exchange membrane were found to be superior to those carried out in an undivided cell.

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