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In situ Oxidative degradation of formaldehyde with hydrogen peroxide electrogenerated on the modified graphites

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The cathodic reduction of oxygen and the degradation of formaldehyde with hydrogen peroxide electrogenerated *in situ* was studied at graphite and modified graphite as cathodes. The peak current of the cathodic reduction of oxygen increased significantly when anodically treated graphite and graphite modified with 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrine cobalt (Co(II)OTP) were used as cathodes, respectively. The current density for the oxidative degradation of formaldehyde was significantly increased when graphite was replaced by anodized graphite as the cathode. Using anodized graphite as cathode, the degradation fractions of the formaldehyde were 99.6 and 98.3% in divided and undivided cells, respectively.

1. Introduction

Formaldehyde is a potential problem in waste waters from various industrial processes and presents a particularly difficult problem in commercial aqueous formaldehyde solutions used for the production of condensation resins [1]. Normal microorganisms die in the presence of formaldehyde, therefore its concentration in waste streams must be decreased by pretreatment before the waste water can be treated in plants by biological clarification. Hydrogen peroxide is a good oxidant for the pretreatment of formaldehyde [1–6], because hydrogen peroxide is converted into oxygen and water which have no toxicity in the subsequent treatment of the waste water. With natural graphite as the cathode, hydrogen peroxide is electrogenerated by the reduction of oxygen and then used for the degradation of formaldehyde *in situ* [7]. In a typical example the concentration of formaldehyde was diminished from 1000 to 2 p.p.m., destroying over 99% of the formaldehyde.

Although the fraction of degraded formaldehyde was large, the limiting current density for producing hydrogen peroxide was less than $0.5\,\mathrm{mA\,cm^{-2}}$ due to the limited concentration of oxygen dissolved in the aqueous phase [7]. The current density for the reduction of oxygen can be promoted by increasing the partial pressure of oxygen [8]. The current density can also be improved by modifying the surface of the cathode. For the reduction of oxygen, modifications of two kinds have been reported [9–22]. First, anodically treated graphite significantly increased the oxygen reduction current density since the active functional groups, quinone-like groups, increased [9–12]. Second, the current density for the production of hydrogen peroxide also increased when the cathode was modified by adsorption of compounds containing quinone-like functional groups [11–14] and metal porphyrines [15–22]. The main pathway for the reduction of oxygen was reported to be a four-electron mechanism resulting in water when the cathodic surface was modified by the adsorption of Fe porphyrine [15, 16]. The main product was hydrogen peroxide when the cathodic surface was modified with Co porphyrine [15, 17, 19–22]. However, the factors affecting the peak current density of oxygen reduction in the anodized graphite and graphite modified by the metal porphyrines have not been systematically studied.

The cathodic reduction of oxygen and degradation of formaldehyde on modified graphites is described in this work. The degradation fraction of formaldehyde, the current efficiency, and the distribution of products were determined. The graphite surfaces were modified by anodic treatment and the adsorption of metal porphyrine.

2. Experimental details

2.1. *Anodic treatment of graphite*

The graphite was polished with fine emery paper and washed with distilled water in an ultrasonic cleaner. The graphite was then treated at pH 6.88 in a buffer solution with an anodic current. The anodic treatment of graphite was done at a constant potential and terminated when a preset time or charge was attained. Then the anodically treated graphite was treated by a constant cathodic potential 1.5 V vs Ag/AgCl/NaCl(3 M) for one minute.

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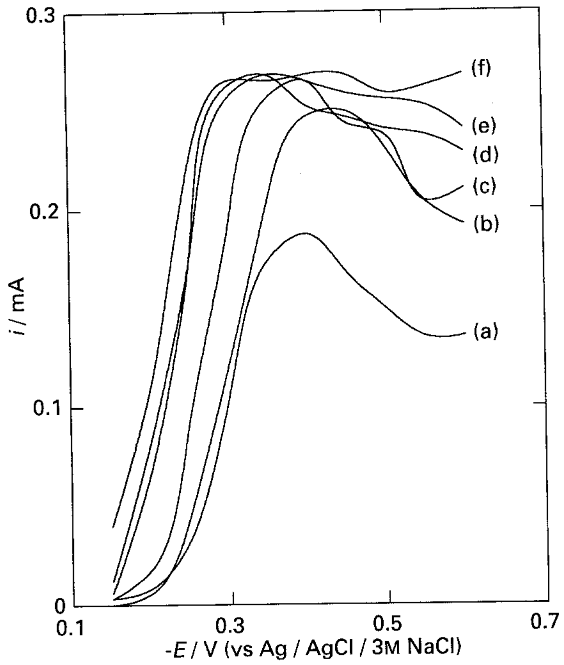

Fig. 1. LSV of the cathodic reduction of oxygen on the anodization graphite. Cathode: graphite anodized in pH 6.88 phosphate buffer solution at 1.8 V (vs Ag/AgCl/3 M NaCl solution), area of cathode = 0.25 cm^2, scanning rate = 100 mV s^{-1}, pH 13, oxygen saturated at room temperature. Anodization time: (a) 0, (b) 1/12, (c) 1, (d) 3, (e) 5 and (f) 10 min.

2.2. *Modification of graphite with metal porphyrine*

The graphite was polished and cleaned as above. The graphite was dried in air and dipped in a metal porphyrine chloroform solution at a specific concentration for a set period. The graphite was then taken out and dried in air.

2.3. *Linear sweep voltammetry (LSV)*

The LSV experiments were carried out in an undivided cell. The graphite, anodized graphite and graphite adsorbed with metal porphyrines were each used as the working electrode. A platinum wire served as the counter electrode, and the reference electrode was Ag/AgCl/NaCl (3 M) aqueous solution. Before the run, oxygen was sparged into the electrolyte until the solution was saturated. The scanning rate and range of cathodic potential for the LSV experiment were controlled with an electrochemical analyser (BAS 100B). All potentials stated in this paper are relative to the reference electrode, Ag/AgCl/NaCl (3 M) aqueous solution.

2.4. *Degradation of formaldehyde with the hydrogen peroxide electrogenerated* in situ

The degradation of formaldehyde with hydrogen peroxide electrogenerated *in situ* was carried out as previously described [7] using three types of working electrode. Formaldehyde concentration was determined by the light adsorption of a chromotropic acid–formaldehyde coloured complex at 575 nm [3]. The concentration of formic acid was determined by iodometric titration [23].

Table 1. Effect of anodization time of the anodic treatment of graphite on the cathodic reduction of oxygen. Cathode: graphite anodized in pH 6.88 phosphate buffer solution at 1.8 V (vs Ag/AgCl/3 M NaCl solution), area of cathode = 0.25 cm^2, scanning rate: 100 mV s^{-1}, pH 13, oxygen saturated at room temperature

Anodization time/min	*Peak current density of LSV/mA cm^{-2}*	*Cathodic decomposition potential of O_2/V (vs Ag/AgCl/3 M NaCl)*
0	0.75	0.24
1/12	1.00	0.23
1	1.06	0.21
3	1.07	0.14
5	1.07	0.14
10	1.07	0.12

3. Results and discussion

3.1. *Cathodic reduction of oxygen to hydrogen peroxide on anodized graphite*

3.1.1. *Effect of period anodization.* The graphite was treated in a phosphate buffer solution at pH 6.88. The treatment potential was 1.8 V. The LSV results of the reduction of oxygen are shown in Fig. 1 for various periods of anodization. The oxygen reduction current increased to a maximum value (peak current) when the potential of oxygen reduction increased (Fig. 1). The peak reduction currents on anodized graphites were larger than that of graphite without anodic treatment. Changing the anodization time from 0 to 3 min increased the peak current from 0.75 to 1.07 mA cm^{-2} (Table 1). The charge passed during anodization of graphite was 55.6 C dm^{-2} when the period of anodization was 3 min. When the duration of anodization exceeded 1 min, the peak current remained constant. Garten and Wiess [24] proposed that the active functional groups for oxygen reduction on graphite were quinone-like. It is also known that anodic oxidation of isotropic carbon increased the number of quinone/hydroquinone groups on the surface [25]. Thus the number of quinone-like functional groups on the graphite surface increase and cause an increase in the peak current when the charge of the anodically treated graphite increases.

As illustrated in Table 1, the decomposition voltage for oxygen reduction decreased from 0.24 to 0.14 V when the graphite anodization period increased from 0 to 3 min. With further increase of the anodization time to 10 min the decomposition voltage decreased slightly to 0.12 V. Thus, the electrocatalytic effect on the cathodic reduction of oxygen to hydrogen peroxide was promoted when the graphite was anodized. Similar results obtained in the literature indicated that the peak potential of the electroreduction of oxygen was shifted about 200 mV in the positive direction and the peak current increased

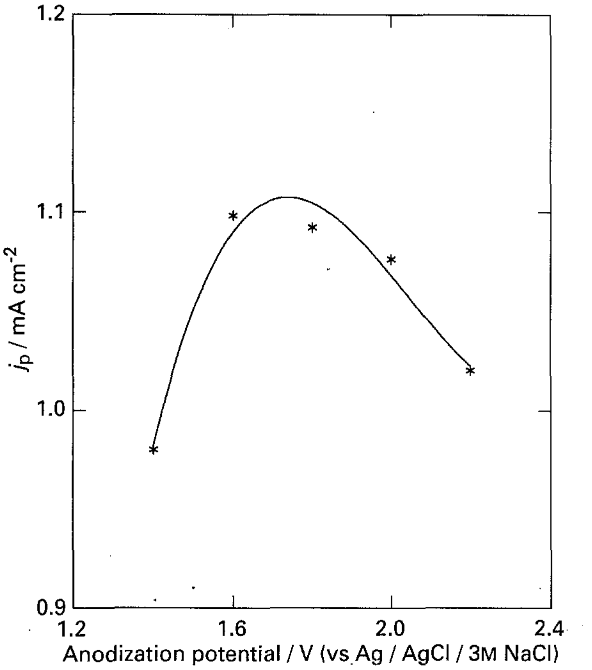

Fig. 2. Effect of anodization potential on the peak current of the cathodic reduction oxygen. Cathode: graphite anodized in pH 6.88 phosphate buffer solution for 55.6 C dm^{-2}, area of cathode = 0.25 cm^2, scanning rate = 100 mV s^{-1}, pH 13, oxygen saturated at room temperature.

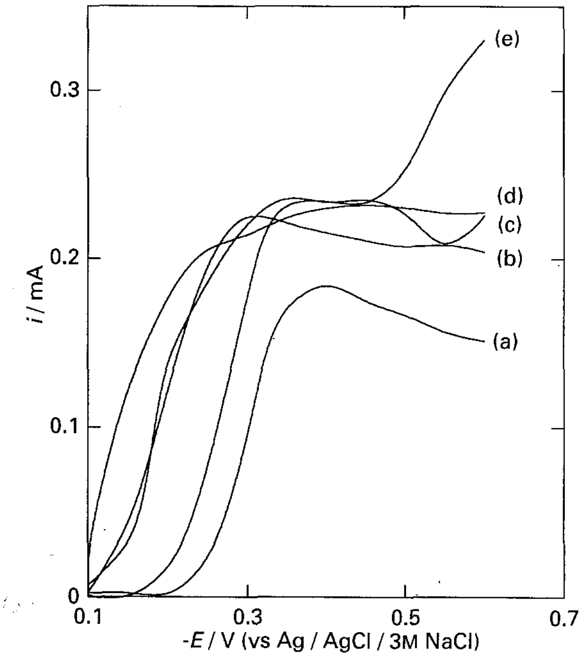

Fig. 3. LSV of the cathodic reduction of oxygen on the graphite adsorbed with metal-TPP. Cathode: graphite adsorbed with 0.5 mM metal-TPP for 5 min, area of cathode = 0.25 cm^2, scanning rate = 100 mV s^{-1}, pH 13, oxygen saturated at room temperature. Metal–TPP: (a)——, (b) Ni(II)TPP, (c) Mn(III)TPP, (d) Co(II)TPP and (e) Fe III) TPP.

by about 30% when the glassy carbon was anodized [11].

3.1.2. Effect of anodization voltage. Increasing the anodization voltage from 1.4 to 1.6 V caused the oxygen reduction peak current to increase from 0.98 to 1.10 mA cm^{-2} when the charge passed during the anodic treatment was stopped at 55.6 C dm^{-2} (Fig. 2). This indicates that the surface concentration of active functional groups on the graphite surface increased as the anodization voltage increased. The peak current decreased slightly when the anodization voltage was greater than 1.6 V. With the anodization voltage further increased to 2.2 V, the peak current decreased to 1.02 mA cm^{-2} as illustrated in Fig. 2. It is possible that active functional groups on the graphite surface were destroyed by over oxidation when the anodization voltage exceeded 1.6 V.

3.2. *Cathodic reduction of oxygen to hydrogen peroxide on graphite modified with metal porphyrines*

3.2.1. Effect of the type of metal porphyrines. Graphite modified with metal–5,10,15,20-tetraphenyl-21H,23H–porphyrine (TPP) and metal–2,3,7,8,12,13,17,18-octaethyl-21H,23H–porphyrine (OTP), respectively, were used as cathodes. Using graphite modified with Co(II)TPP, Ni(II)TPP, Mn(III)TPP, and Fe(III)TPP as cathodes for oxygen reduction resulted in an increase in the peak currents and a decrease in the decomposition voltages as shown in Fig. 3. The experimental results revealed that the peak current increased from 23.3 to 28.8% when graphites with adsorbed metal–TPP were used (Table 2). The cathodic decomposition potential of oxygen reduction decreased from 0.24 to 0.09 V when graphite was replaced with graphite treated with Co(III)TPP as illustrated in Table 2.

The peak current and the decomposition voltage were not significantly altered when Ni(II)OTP and Cu(II)OTP were used to modify the graphite as shown in Fig. 4. The peak current, however, sharply increased, and the cathodic decomposition voltage decreased, when graphite adsorbed with Co(II)OTP was used. The experimental results indicated that the oxygen reduction was significantly affected by the kinds of metal in the metal–OTP used for modification of the graphite.

In comparison with natural graphite, the decomposition voltages for the cathodic reduction of oxygen on graphite modified with metal–TPP and metal–OTP significantly decreased except for Fe(III)TPP, Ni(II)OTP, and Cu(II)OTP as shown in Table 2.

Table 2. Effect of type of metal porphines adsorbed on the graphite on the cathodic reduction of oxygen. Cathode: graphite adsorbed with 0.5 mM metal-porphine, adsorption time: 5 min, area of cathode = 0.25 cm^2, scanning rate: 100 mV s^{-1}, pH 13, oxygen saturated at room temperature

Metal-porphyrines adsorbed on graphite	*Peak current density of LSV/mA cm^{-2}*	*Cathodic decomposition potential of O_2/V (vs Ag/AgCl/3 M NaCl)*
–	0.73	0.24
Ni(II)TPP	0.93	0.13
Mn(III)TPP	0.94	0.14
Co(II)TPP	0.90	0.09
Fe(III)TPP	0.94	0.21
Ni(II)OTP	0.69	0.23
Cu(II)OTP	0.73	0.21
Co(II)OTP	1.01	0.09

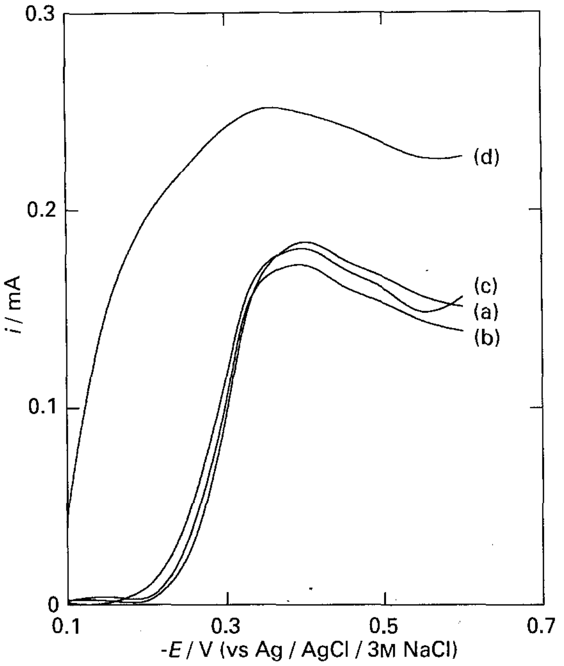

Fig. 4. LSV of the cathodic reduction of oxygen on the graphite adsorbed with metal–OTP. Cathode: graphite adsorbed with 0.5 mM metal–OTP for 5 min, area of cathode = 0.25 cm^2, scanning rate = 100 mV s^{-1}, pH 13, oxygen saturated at room temperature. Metal-OTP: (a) ——, (b) Ni(II)OTP, (c) Cu(II)OTP and (d) Co(II)OTP.

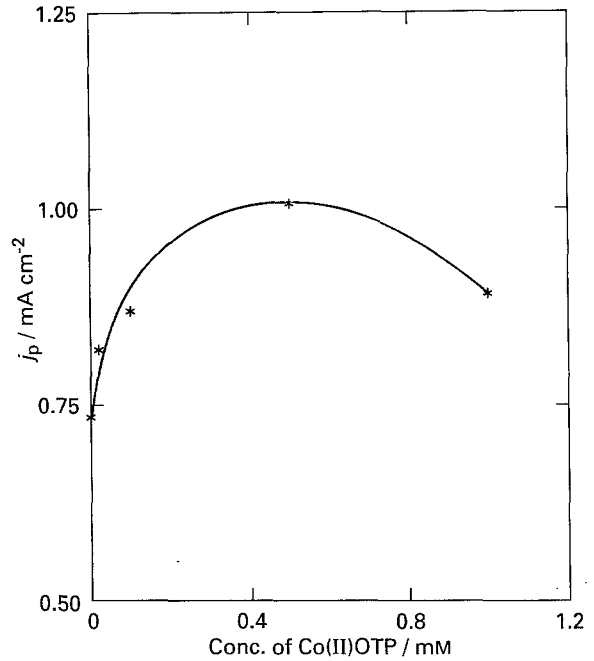

Fig. 5. Effect of adsorbed concentration of Co(II)OTP on the peak current density of the cathodic reduction of oxygen. Cathode: graphite adsorbed with Co(II)OTP for 5 min, area of cathode = 0.25 cm^2, scanning rate = 100 mV s^{-1}, pH 13, oxygen saturated at room temperature.

The minimum decomposition voltage of oxygen reduction was 0.09 V when graphites modified with Co(II)TPP and Co(II)OTP, respectively, were used as cathodes. The peak current density of oxygen reduction on graphite modified with metal porphyrines increased except for Cu(II)OTP and Ni(II)OTP. The maximum peak current density obtained was 1.01 mA cm^{-2} when graphite adsorbed with Co(II)OTP was used (Table 2). Hence the Co(II)OTP modified graphite exhibited the best electrocatalytic effects for the cathodic reduction of oxygen to hydrogen peroxide relative to graphite modified with other metal porphyrines. The cathodic reduction of oxygen on the Co–TMPP (cobalt tetramethoxyphenyl porphyrine) modified XC-72 studied by Scherson *et al.* on a rotating disc electrode revealed that the limiting current density increased about 100% at 4900 r.p.m. [17].

3.2.2. Effect of the concentration of Co(II)OTP adsorbed on the graphite. Using graphite modified with Co(II)OTP as cathode, the peak current density for oxygen reduction increased from 0.75 to the maximum value, 1.01 mA cm^{-2} when the concentration of Co(II)OTP adsorbed on the graphite was increased from 0 to 0.5 mM (Fig. 5). With the concentration of Co(II)OTP increased further to 1.0 mM, the peak current density decreased to 0.89 mA cm^{-2}. This may be due to the fact that the Co(II)OTP adsorbed on the graphite was no longer monomeric as the concentration of Co(II)OTP adsorbed exceeded 0.5 mM. A similar result was reported by Antoniadou *et al.* [20].

3.2.3. Effect of period of adsorption. Increasing the period of adsorption from 0 to 5 min resulted in an increase in peak current density from 0.73 to 1.01 mA cm^{-2} when the graphite adsorbed with 0.5 mM Co(II)OTP was used as cathode (Fig. 6). The peak current density decreased slightly to 0.90 mA cm^{-2} when the period of adsorption of Co(II)OTP was increased further to 30 min. Possibly a multiple layer of Co(II)OTP adsorbed on the graphite surface decreased the electrocatalytic effects as described above.

3.3. *Cathodic reduction of oxygen to hydrogen peroxide on graphite modified by anodic treatment and adsorption of Co(II)OTP*

The graphite was treated at 1.6 V anodic current until 55.6 C dm^{-2} passed and Co(II)OTP was then adsorbed for 5 min. The peak current density of oxygen reduction decreased from 1.10 to 0.98 mA cm^{-2} when the concentration of Co(II)OTP adsorbed on the anodization graphite increased from 0 to 0.5 mM as shown in Fig. 7. In comparison with anodized graphite, the cathodic decomposition voltage on the anodization graphite adsorbed with 0.5 mM Co(II)OTP decreased from 0.16 to 0.09 V. These results indicate that the cathodic reduction of oxygen on graphite modified with an anodic charge and then adsorbed with Co(II)OTP exhibited similar electrocatalytic character when the natural graphite adsorbed with Co(II)OTP was used. The active functional groups, quinone-like, generated with the anodization of graphite, may be covered by Co(II)OTP when the anodized graphite was further treated with Co(II)OTP.

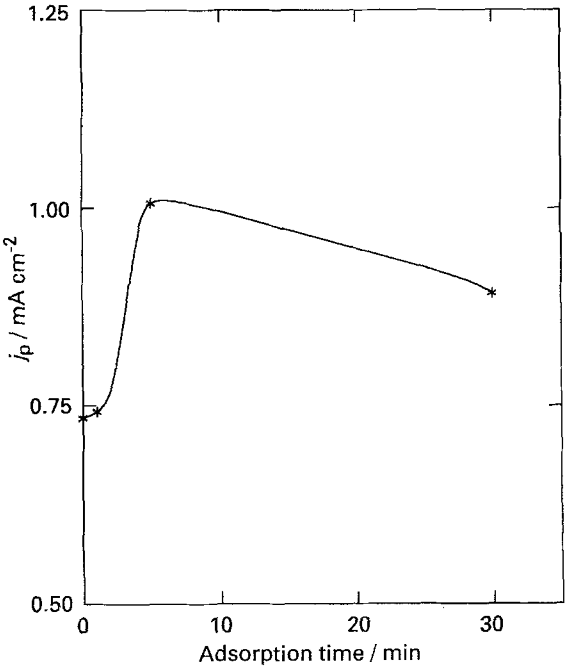

Fig. 6. Effect of adsorption time on the peak current density of the cathodic reduction of oxygen. Cathode: graphite adsorbed with 0.5 mM Co(II)OTP, area of cathode = 0.25 cm^2, scanning rate = 100 mV s^{-1}, pH 13, oxygen saturated at room temperature.

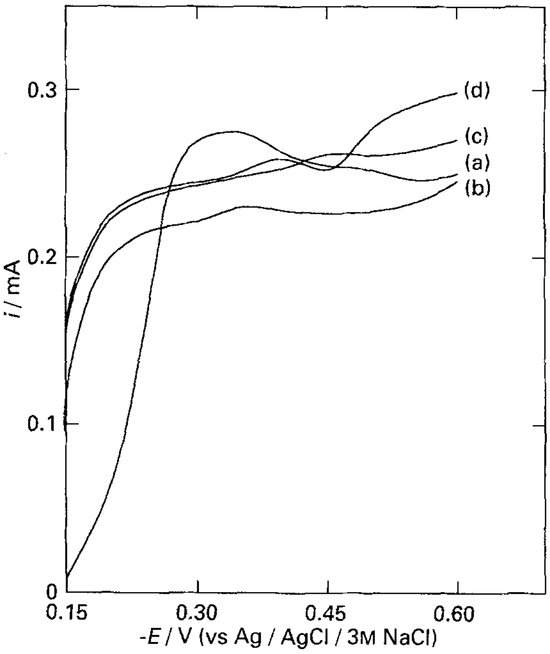

Fig. 7. LSV of the cathodic reduction of oxygen on the anodization graphite adsorbed with Co(II)OTP. Cathode: graphite anodized in pH 6.88 phosphate buffer solution at 1.6 V (vs Ag/AgCl/3 M NaCl solution) for 55.6 C dm^{-2} and adsorbed with Co(II)OTP for 5 min, area of cathode = 0.25 cm^2, scanning rate = 100 mV s^{-1}, pH 13, oxygen saturated at room temperature. [Co(II)OTP] in chloroform: (a) 0, (b) 0.1, (c) 0.5 and (d) 1.0 mM.

3.4. *Oxidative degradation of formaldehyde with hydrogen peroxide electrogenerated in situ*

3.4.1. Effect of current density. The oxidative degradation of formaldehyde by hydrogen peroxide electrogenerated *in situ* in the alkaline solution proceeds as follows [7]

$$(O_2)_{aq} + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^- \quad (1)$$

$$2HCHO + HO_2^- + OH^- \rightarrow 2HCO_2^- + H_2O + H_2\uparrow \quad (2)$$

The main reaction on the cathodic surface was reduction of oxygen dissolved in the aqueous phase to produce hydrogen peroxide. The electrogenerated hydrogen peroxide produced oxidative degradation of formaldehyde in the bulk solution. With increase in the current density from 0.5 to 0.75 mA cm^{-2}, the fraction of formaldehyde degraded changed slightly when anodized graphite was used as cathode (Fig. 8). With further increase of the current density to 1.25 mA cm^{-2}, the fraction of formaldehyde degraded decreased from 52.2 to 38.7%. This shows that the limiting current density for the cathodic reduction of dissolved oxygen was about 0.75 mA cm^{-2}. The side reactions of the *in situ* oxidative degradation of formaldehyde, hydrogen evolution and reduction of hydrogen peroxide to water, increased with current density larger than 0.75 mA cm^{-2}.

As shown in Fig. 9, the concentration of formaldehyde was degraded from 500 to 2 p.p.m. when 1.5 F mol^{-1} HCHO was passed. The degradation fraction and the current efficiency were 99.6% and 69.0%, respectively. The main product of the oxidative degradation of formaldehyde with hydrogen peroxide electrogenerated *in situ* was formic acid (Fig. 9). Formic acid was subsequently oxidized by hydrogen peroxide to carbon dioxide, which resulted in a slight decrease of formic acid concentration when the passed charge exceeded 1.0 F per mole of HCHO.

3.4.2. Effect of graphite modification. As illustrated in Fig. 8, the maximum degradation fraction of formaldehyde was 51.2% when natural graphite was used as cathode and the current density was 0.5 mA cm^{-2}. Using graphite treated with 55.6 C dm^{-2} anodic charge, the maximum degradation fraction was 52.2% with a current density of 0.75 mA cm^{-2}. The maximum degradation increased slightly and the current density increased by 50% when natural graphite was replaced by anodized graphite. Increase in current density resulted in a decreased treatment time for wastewater containing formaldehyde. For example, for the same experimental conditions, the period of oxidative degradation from 500 to 2 p.p.m. were 132 and 198 min when anodized graphite and natural graphite were used as cathodes, respectively. The corresponding current efficiencies had no significant difference when 500 p.p.m. formaldehyde was degraded to 2 p.p.m. as shown in Fig. 9 and in previous results [7].

With graphite treated with Co(II)OTP as cathode, the maximum formaldehyde degradation fraction was 44.0% with a current density of 0.75 mA cm^{-2} (Fig. 8). Although the degradation fraction decreased, the limiting current density increased when natural graphite was replaced by graphite modified with

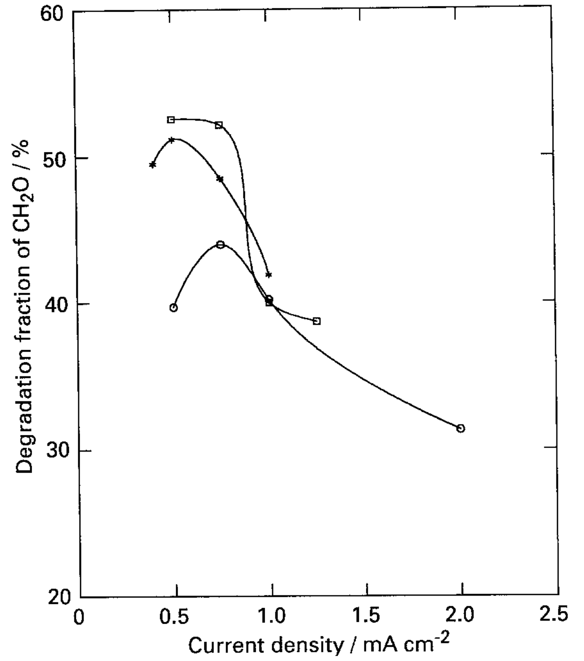

Fig. 8. Effect of current density on the degradation fraction of formaldehyde. Cathodes: (*) natural graphite; (□) graphite anodized in the pH 6.88 phosphate buffer solution at 1.6 V (vs Ag/AgCl/3 M NaCl solution) for 55.6 C dm^{-2}, (○) graphite adsorbed with 0.5 mM Co(II)OPT for 5 min, area of cathode = 50.4 cm^2, temperature = 45°C, oxygen sparging rate = 5 cm^3 s^{-1}, pH 13, $Q = 0.5$ F mol^{-1} of CH_2O, $[CH_2O]_i = 500$ p.p.m. Key: (*) graphite, (□) anodization graphite and (○) graphite adsorbed with Co(II)OTP.

Co(II)OTP as cathode. These results may be due to the increase of side reactions (hydrogen evolution and reduction of hydrogen peroxide) on the cathode when the Co(II)OTP modified graphite was used.

3.4.3. Effect of the electrolysis cell. Using anodized graphite as cathode, the oxidative degradation of formaldehyde proceeded in an undivided cell and the concentration of formaldehyde decreased from 500 to 8.5 p.p.m. when 1.5 F per mole of HCHO was passed (Fig. 10). Under the same experimental conditions, the concentration of formaldehyde decreased from 514 to 2 p.p.m. when the electrolysis cell was divided by a sintered glass frit. The degradation fraction were as 98.3 and 99.6% when the process took place in an undivided and a divided cell, respectively. The effect of the electrolysis cell on the oxidative degradation of formaldehyde was insignificant.

4. Conclusions

Using anodization graphite as cathode, the peak current density and decomposition voltage for oxygen reduction were affected by the anodization voltage and duration. The maximum peak current density was 1.10 mA cm^{-2} when the graphite was treated at 1.6 V with 55.6 C dm^{-2}. The factors affecting the peak current and decomposition voltage of the cathodic reduction of oxygen were the duration of adsorption and the types and concentration of the metal porphyrines used to treat the graphite. Under the same experimental conditions, the period of oxidative degradation of formaldehyde was reduced by 33.3% when natural graphite was replaced by anodized graphite as cathode. The concentration of formaldehyde was effectively degraded from 514 to 2 p.p.m. in the divided cell when anodized graphite was used. The effect of the type of electrolysis cell on the oxidative degradation of formaldehyde with hydrogen peroxide electrogenerated *in situ* was slight.

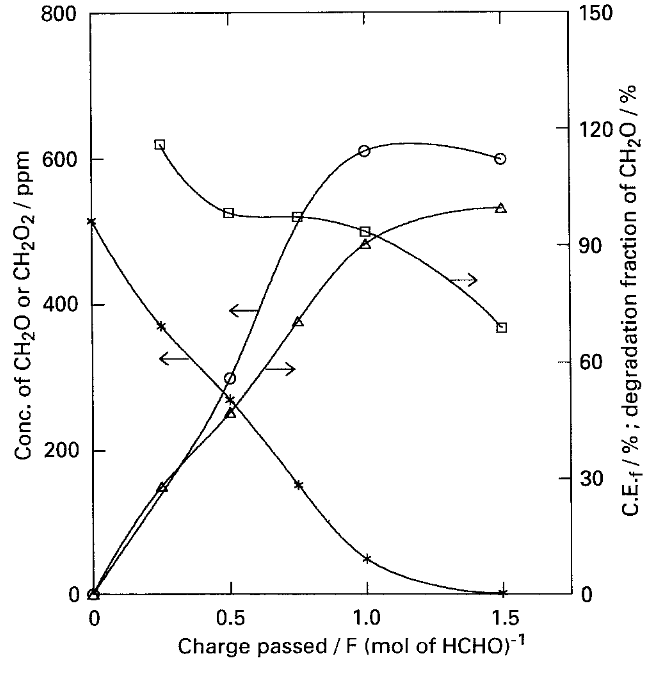

Fig. 9. Effect of charge passed on the oxidative degradation of formaldehyde. Cathodes: graphite anodized in the pH 6.88 phosphate buffer solution at 1.6 V (vs Ag/AgCl/3 M NaCl solution) for 55.6 C dm^{-2}, current density = 0.75 mA cm^{-2}, area of cathode = 50.4 cm^2, temperature = 45 °C, oxygen sparging rate = 2 cm^3 s^{-1}, pH 13, $[CH_2O]_i = 500$ p.p.m. Key: (△) degradation fraction of CH_2O, (*) conc. of CH_2O, (○) conc. of CH_2O_2 and (□) CE_f.

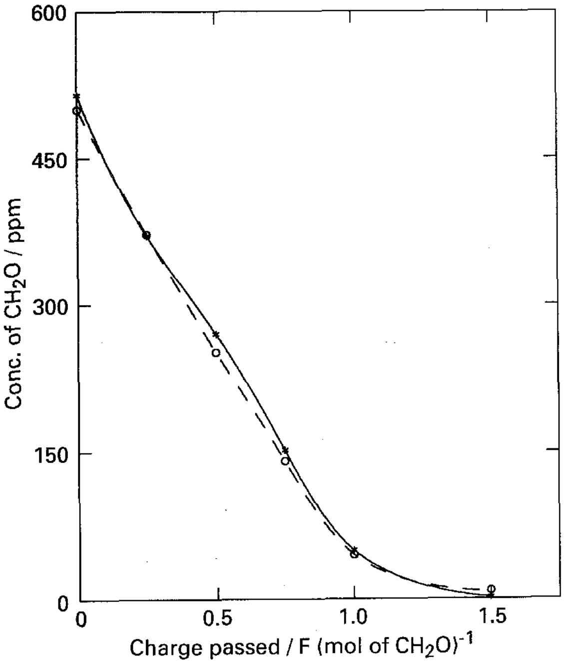

Fig. 10. Effect of charge passed on the concentration of formaldehyde. Cathodes: graphite anodized in the pH 6.88 phosphate buffer solution at 1.6 V (vs Ag/AgCl/3 M NaCl solution) for 55.6 C dm^{-2}, current density = 0.75 mA cm^{-2}, area of cathode = 50.4 cm^2, temperature = 45 °C, oxygen sparging rate = 2 cm^3 s^{-1}, pH 13, $[CH_2O]_i$ = 500 p.p.m. Key: (∗) divided cell and (○) undivided cell.

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