

Electrocatalytic oxidation of 2-chlorophenol on a composite PbO₂/polypyrrole electrode in aqueous solution

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The electrocatalytic oxidation of 2-chlorophenol on a composite PbO₂/polypyrrole (PPy) electrode was carried out in 0.1 M H₂SO₄ solution. The composite PbO₂/PPy electrode was developed by the codeposition of polypyrrole and PbO₂ microparticles on the PbO₂/SnO₂/Ti substrate. The PbO₂ microparticles and polypyrrole in the composite electrode were observed to be hydrophilic active-sites and hydrophobic inactive-sites, respectively. The results indicated that the conversion of 2-chlorophenol and the efficiency of electrooxidation were improved on the hydrophobic-modified PbO₂/PPy electrode. The performance for electrooxidation of 2-chlorophenol on the composite PbO₂/PPy electrode was better than that on Pt or PbO₂/SnO₂/Ti electrodes. The thicker the composite (PbO₂/PPy) layer, the more active-sites in the composite electrode and the more 2-chlorophenol could be oxidized.

1. Introduction

Although polypyrrole (PPy) was first prepared at the beginning of the century it was not until the synthesis of continuous films by anodic oxidation reported in 1979 [1] that interest in PPy began to develop. This discovery prompted a large body of literature related to the various properties of this conducting polymer. PPy has found particular utility in the rapidly expanding field of chemically modified electrodes [2]. Polymer films are frequently more effective than monolayers of either adsorbed or covalently bound catalysts since they display better stability and hydrophobicity. These catalysts may be incorporated as either counter ions balancing the positive charge on the oxidized polymer, or as microparticles or pendant groups attached to the polymer matrix, either by utilizing functionalized monomers or else through chemical modification of an already deposited PPy film.

Substituted phenols are thought to be environmentally important in view of their toxicity and possible accumulation in the environment [3–5]. Vigorous research has been devoted to the development of various treatment technologies: for example, adsorption, demineralization and photolytic processes for phenolic pollution removal from waters and wastewaters. Less energy requirement with the electrochemical method yields potential savings in decomposition costs. Studies are currently being directed in this area [6].

Modified electrodes are finding increasingly impor-

tant applications in industrial processes. In addition to its hydrophobicity, the composite-plated PTFE/Ni was also reported [7, 8] to be highly electroconductive, and mechanically and electrochemically stable. PbO₂ is favoured as an electrocatalytic material in view of its high electrical conductivity, large oxygen overpotential, and chemical inertness in applications for electrolysis and electrosynthesis. The modification by PTFE on a PbO₂ electrode with its beneficial effect of hydrophobicity toward electrooxidation of organic substrates has been described [9]. The PbO₂ and PTFE in the composite PTFE/PbO₂ electrode exhibited hydrophilic-active sites and hydrophobic-inactive sites, respectively. PPy has been modified with a variety of metals, including Pd, Pt, Pb, Cu, Ni, Sn and Au [10–13]. However, no literature has described a PPy electrode modified via the codeposition of PbO₂ microparticles and polypyrrole. The composite PbO₂/PPy electrode is described in the present work.

This paper describes an investigation of the electrocatalytic oxidation of 2-chlorophenol on a composite PbO₂/PPy electrode in aqueous solution. The composite PbO₂/PPy electrode is developed via the codeposition of polypyrrole and PbO₂ microparticles on the PbO₂/SnO₂/Ti substrate. To facilitate comparison, platinum electrodes, PbO₂ electrodes and PbO₂/PPy electrodes are also used and characterized by cyclic voltammetry in blank and 2-chlorophenol solutions.

2. Experimental details

All chemicals were of analytical reagent grade and used without further purification. 2-Chlorophenol, acetonitrile, and pyrrole were purchased from Janssen

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Chemicals. All other chemicals were from Fisher Scientific, or Aldrich Chemicals. Water was distilled and purified in a NANO pure-II system (Barnstead).

2.1. Preparation of SnO_2/Ti electrode on titanium substrate

A $2\text{ cm} \times 3\text{ cm} \times 0.5\text{ cm}$ titanium plate was first degreased with a mixture of detergent and kieselguhr (3:1 by mass), rinsed with deionized water and then etched in 6 M HCl solution at 90 to 95 °C for 2 h, followed by formation of an inner layer of SnO_2 . This inner layer was formed by baking the etched plate at 60 °C for 4 h after dipping in a solution consisting of 20 g of $\text{SnCl}_4 \cdot \text{H}_2\text{O}$, 20 ml of *n*-butanol and 1 ml of HCl. After five dips and bake cycles, the plate was baked at 400 °C for 5 min in a furnace (Nabertherm) under 250 ml min^{-1} of air flow [14].

2.2. Preparation of $\text{PbO}_2/\text{SnO}_2/\text{Ti}$ electrode on SnO_2 substrate

In the PbO_2 -deposition cell, the prepared SnO_2/Ti electrode (3.6 cm^2), a copper sheet (4 cm^2) and a saturated calomel electrode (SCE) were employed as the working, counter and reference electrodes, respectively. The temperature and current density were controlled at 60 °C and 10 mA cm^{-2} , respectively, by a thermostat (Eyela, PS-60) and a potentiostat (Model HA310, Hokuto, Denko Ltd). PbO_2 was electrodeposited for 30 min on SnO_2/Ti substrate in a solution containing 350 g dm^{-3} of $\text{Pb}(\text{NO}_3)_2$, 30 g dm^{-3} of $\text{Cu}(\text{NO}_3)_2$, 1 g dm^{-3} of $\text{Pb}(\text{CH}_3\text{COO})_2$ and 5 g dm^{-3} of PbCO_3 [14]. The SP electrode is shown in Fig. 1(a).

2.3. Preparation of PbO_2 microparticles

The electroactive PbO_2 microparticles were obtained by the following procedures. PbO_2 was electro-

deposited as described above except for the platinum substrate being used. The PbO_2 film was then scratched from the Pt substrate and ground to 1–3 μm particle size, measured by scanning electron microscopy (SEM).

2.4. Preparation of composite PbO_2/PPy electrode on $\text{PbO}_2/\text{SnO}_2/\text{Ti}(\text{SP})$ substrate

In the PbO_2/PPy -codeposition cell, the prepared $\text{PbO}_2/\text{SnO}_2/\text{Ti}$ electrode (3.0 cm^2), a platinum sheet (3.0 cm^2) and a saturated calomel electrode (SCE) were employed as the working, counter and reference electrodes, respectively. The temperature was controlled at 30 °C by a thermostat (Eyela, PS-60). The current density (or potential) was controlled at 1 mA cm^{-2} (or in the range of 0.5–1.5 V) by a potentiostat (model HA310, Hokuto, Denko Ltd). The composite PbO_2/PPy film was electrodeposited for 5 min on $\text{PbO}_2/\text{SnO}_2/\text{Ti}$ substrate in a solution containing 100 ml of acetonitrile, 0.01–0.1 M of pyrrole, 0.1 M LiClO_4 and 1.5 g of PbO_2 microparticles. PbO_2 was then electrodeposited at 10 mA cm^{-2} on the PbO_2/PPy electrode for 20 min in the solution described above. The electrode was named a composite PbO_2/PPy electrode (SPCP). The SPCP electrode is shown in Fig. 1(b).

2.5. Electrocatalytic oxidation of 2-chlorophenol

The electrocatalytic oxidation of 2-chlorophenol was carried out in a batch Pyrex reactor. The reactor was cylindrical and of approximately 150 ml capacity with a magnetic stirrer. The reactor was filled with 100 ml of 2-chlorophenol solution of known concentration in 0.1 M H_2SO_4 . In the electrooxidation cell, the composite PbO_2/PPy electrode (3.0 cm^2), a platinum sheet (3.0 cm^2) and a saturated calomel electrode (SCE) was employed as the working, counter and reference electrodes, respectively. The temperature was controlled at 25 °C by a thermostat (Eyela, PS-60). The current density and the concentration of 2-chlorophenol were in the range 0.5–3.0 mA cm^{-2} and 60–1250 mg dm^{-3} , respectively. The current was controlled by a potentiostat (model HA310, Hokuto, Denko Ltd). At intervals during the reaction, a small portion of the solution was withdrawn from the reactor for residual 2-chlorophenol analysis. Concentrations of 2-chlorophenol were determined by gas chromatography (Hitachi, G-3000). The oxidized products were also analysed by gas chromatography [15]. Electrolytic production of carbon dioxide was confirmed by precipitation as CaCO_3 in a solution saturated with $\text{Ca}(\text{OH})_2$. Carbon dioxide, purged from the test solution during electrolysis, was quantified by adsorption in standard NaOH solutions followed by back titration with standard HCl solution using a phenolphthalein red double indicator. To facilitate comparison, Pt, SP, and SPCP electrodes were also used. These electrodes (1 cm^2) were characterized by cyclic voltammetry in blank and

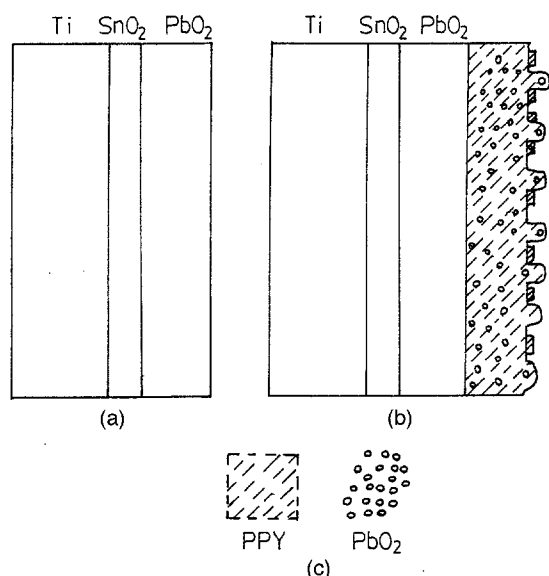


Fig. 1. Representations for structure of electrodes: (a) SP and (b) SPCP.

2-chlorophenol solutions. The electrode potentials for all test solutions were scanned in the range 1000 and 1600 mV vs SCE. The morphologies of these electrodes were examined by SEM.

3. Results and discussion

3.1. Morphology of electrodes

The SEM micrograph of the $\text{PbO}_2/\text{SnO}_2/\text{Ti}$ electrode (SP electrode) is shown in Fig. 2(a). The SP electrode has a pyramid-like morphology. The average crystal size is 8–9 μm . The SEM micrograph of the polypyrrole film on $\text{PbO}_2/\text{SnO}_2/\text{Ti}$ substrate (SPY electrode) is shown in Fig. 2(b). A nodular morphology for the SPY electrode is observed. The average nodule size is 3–4 μm . The morphologies of the SP electrode and SPY electrode are different from a comparison of Fig. 2(a) with 2(b). The SP electrode is seen to be more porous than the SPY electrode. Figure 2(c) shows the SEM micrograph of the composite PbO_2/PPy electrode on the $\text{PbO}_2/\text{SnO}_2/\text{Ti}$ substrate (SPCP electrode). PbO_2 crystals were observed on the surface

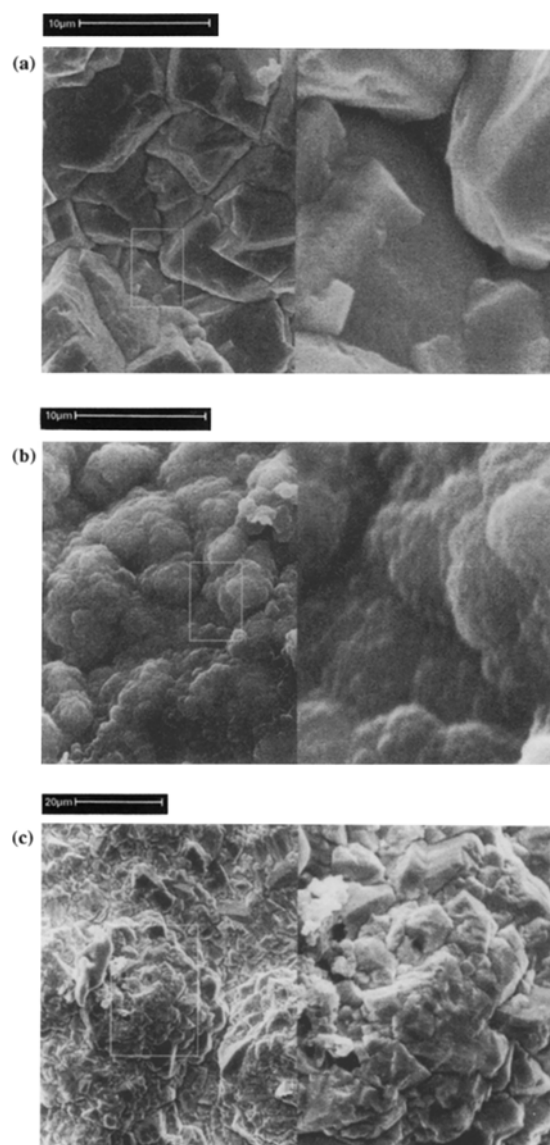


Fig. 2. Morphologies of electrodes: (a) SP, (b) SPY and (c) SPCP.

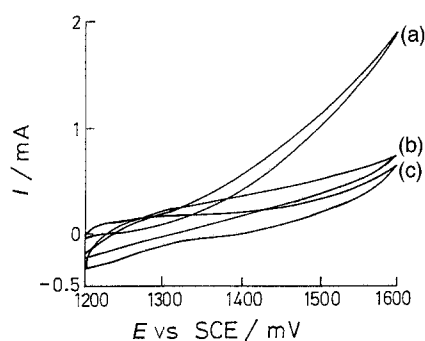


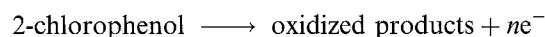
Fig. 3. Cyclic voltammograms in the absence of 2-chlorophenol at different electrodes. Operation conditions: $T = 25^\circ\text{C}$; $V = 100\text{ ml}$. Scan rate: 100 mV s^{-1} . (a) Pt, (b) SP and (c) SPCP.

of the SPCP electrode. The average crystal size of PbO_2 on the surface of the SPCP electrode was 3–4 μm . The SPCP electrode was more compact than the SPY electrode.

3.2. Examination of electrodes by cyclic voltammetry

Figure 3 shows cyclic voltammograms in the absence of 2-chlorophenol at the Pt, SP, and SPCP electrodes. The anodic current in Fig. 3 represents the oxygen evolution reaction. The anodic currents at 1.6 V vs SCE are 1.9, 0.75 and 0.65 mA cm^{-2} for the Pt, SP and SPCP electrodes, respectively. This reveals that the electrocatalytic performance for oxygen evolution lies in the order Pt electrode > SP electrode > SPCP electrode. The cyclic voltammograms of the Pt, SP, and SPCP electrodes in the 150 mg dm^{-3} 2-chlorophenol are shown in Fig. 4. The anodic currents in 150 mg dm^{-3} 2-chlorophenol (Fig. 4) are larger than those in the absence of 2-chlorophenol (Fig. 3) on the same electrode. This indicates that the oxidation of 2-chlorophenol occurs on Pt, SP, and SPCP electrodes. The anodic current in Fig. 4 represents the overall reactions involving oxygen evolution and the oxidation of 2-chlorophenol. The electrooxidation reactions on these electrodes can be written as follows:

Oxidation of 2-chlorophenol



Oxygen evolution

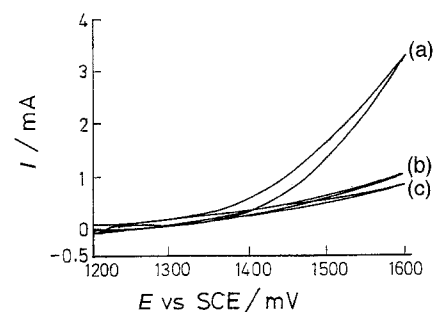
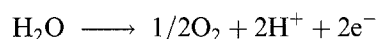


Fig. 4. Cyclic voltammograms in the presence of 2-chlorophenol at different electrodes. Operation conditions: $T = 25^\circ\text{C}$; $V = 100\text{ ml}$. $C_p = 125\text{ mg dm}^{-3}$. Scan rate: 100 mV s^{-1} . (a) Pt, (b) SPCP and (c) SP.

Carbon dioxide, oxalic, maleic, and glyoxylic acids were always detected during the electrocatalytic oxidation of 2-chlorophenol and contributed about 60–90% of the conversion of 2-chlorophenol. Since the reaction products are complicated, the number of electrons involved per mole of 2-chlorophenol is difficult to determine. Therefore, the efficiency of oxidation for 2-chlorophenol is defined as

$$\eta = FV \frac{C_i - C_f}{Q}$$

where F , V , C_i , C_f and Q are Faraday's constant, volume of solution, the initial concentration of 2-chlorophenol, the final concentration of 2-chlorophenol, and the charge passed, respectively.

The anodic currents at 1.6 V vs SCE are 3.3, 1.3 and 1.7 mA cm⁻² on the Pt, SP, and SPCP electrodes, respectively. This implies that the order of the electrocatalytic performance for the overall reaction is Pt electrode > SPCP electrode > SP electrode. The results also confirmed that the electrocatalytic oxidation of 2-chlorophenol on the SPCP electrode is better than that on the SP electrode. Although the anodic current on the Pt electrode is the largest among these electrodes, its efficiency for the oxidation of 2-chlorophenol (data shown in later) is the lowest. In the aqueous solution, 2-chlorophenol is a hydrophobic-reactant while H₂O is a hydrophilic-reactant [16]. The contact angles of water on SPCP and SP electrodes are about 70° and 24°, respectively. This suggests that the hydrophobicity of SPCP electrodes is higher than that of SP electrodes. The oxidation of a hydrophilic-reactant (H₂O) will be inhibited on the hydrophobic electrode (SPCP). In contrast, the oxidation of a hydrophobic-reactant (2-chlorophenol) will be enhanced on the hydrophobic electrode (SPCP).

3.3. Electrooxidation of 2-chlorophenol at SP electrodes

The electrocatalytic oxidation of 2-chlorophenol on the SP electrodes was carried out at various current

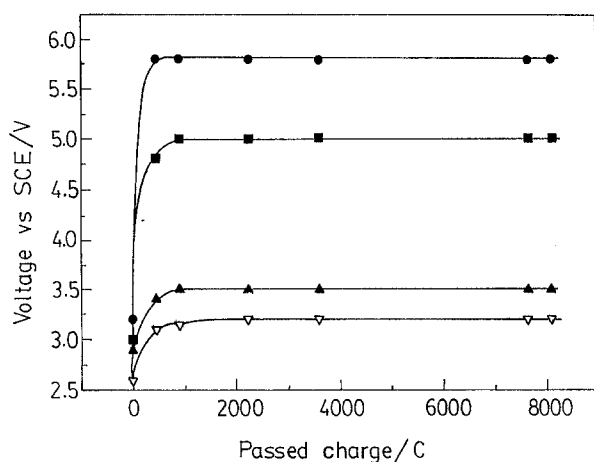


Fig. 5. Dependence of electrolytic voltage on charge passed at various current densities. Operation conditions: electrode: SP; $V = 100$ ml; $T = 25^\circ\text{C}$. Stirring rate: 350 r.p.m.; $C_0 = 125$ mg dm⁻³. Key: (∇) 0.5, (\blacktriangle) 1.0, (\blacksquare) 2.0 and (\bullet) 3.0 mA cm⁻².

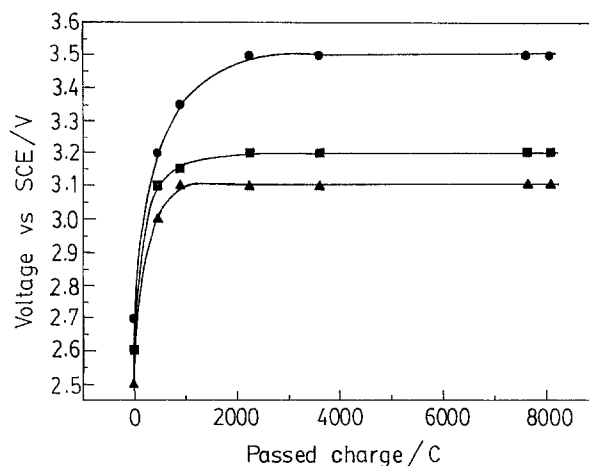


Fig. 6. Dependence of electrolytic voltage on charge passed at various concentrations of 2-chlorophenol. Operation conditions: electrode: SP; $V = 100$ ml; $T = 25^\circ\text{C}$. Stirring rate: 350 r.p.m.; $i = 0.5$ mA cm⁻². Key: (\bullet) 1250, (\blacksquare) 125 and (\blacktriangle) 60 mg dm⁻³.

densities (or concentrations of 2-chlorophenol) (other operation conditions were unchanged). The conversion of 2-chlorophenol and the efficiency of oxidation against charge passed at different current densities were obtained (data not shown here). Both the conversion and the efficiency decreased with increase in applied current density for the same charge passed. This implies that the side reactions (e.g., oxygen evolution) increase as the applied current density increases. The dependence of voltage on charge passed at various current densities is shown in Fig. 5. The voltage increased initially and then remained constant, indicating that SP electrodes are stable. The higher the voltage, the higher the current density. Similarly, the electrocatalytic oxidation of 2-chlorophenol on the SP electrodes was carried out at various concentrations of 2-chlorophenol. The conversion and the efficiency against the charge passed at various concentrations of 2-chlorophenol were also obtained (data not shown here). The conversion decreased with increase in the 2-chlorophenol concentration in the aqueous solution. However, higher efficiency of oxidation was obtained at higher 2-chlorophenol concentration. The dependence of voltage on the charge passed at different concentrations of 2-chlorophenol is illustrated in Fig. 6. This shows that the SP electrodes were stable during the period of oxidation.

3.4. Electrooxidation of 2-chlorophenol at SPCP electrodes

Various SPCP electrodes were obtained via the codeposition of PbO₂ microparticles and polypyrrole under different conditions. Figures 7 and 8 show the dependence of conversion of 2-chlorophenol and efficiency of oxidation on charge passed at various electrodes obtained by the codeposition of PbO₂ microparticles and polypyrrole at different concentrations of pyrrole. These Figures indicate that the conversion of 2-chlorophenol and the efficiency of oxidation increase with increase in pyrrole concentration. The voltage for the codeposition reaction

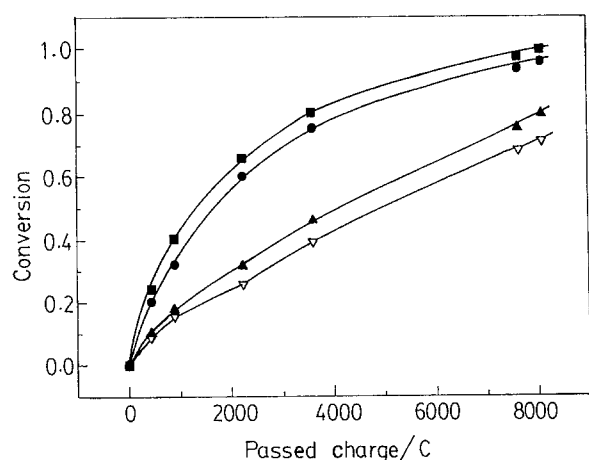


Fig. 7. Plot of the conversion of 2-chlorophenol and the efficiency of oxidation against charge passed at various electrodes obtained by the codeposition of PbO_2 microparticles and polypyrrole at different concentrations of pyrrole. Operation conditions: electrode: SPCP; $V = 100$ ml; $T = 25^\circ\text{C}$. Stirring rate: 350 r.p.m.; $i = 0.5$ mA cm^{-2} ; $C_p = 125$ mg dm^{-3} . Key: (∇) 0.01, (\blacktriangle) 0.05, (\bullet) 0.075 and (\blacksquare) 0.1 M.

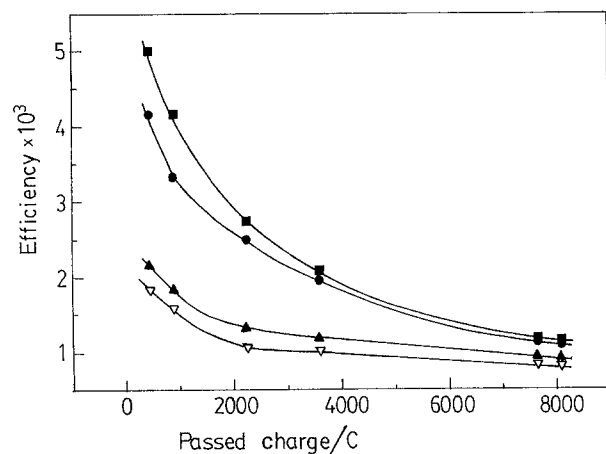


Fig. 8. Plot of the efficiency of oxidation against charge passed at various electrodes obtained by the codeposition of PbO_2 microparticles and polypyrrole at different concentrations of pyrrole. Operation conditions: electrode: SPCP; $V = 100$ ml; $T = 25^\circ\text{C}$. Stirring rate: 350 r.p.m.; $i = 0.5$ mA cm^{-2} ; $C_p = 125$ mg dm^{-3} . Key: (∇) 0.01, (\blacktriangle) 0.05, (\bullet) 0.075 and (\blacksquare) 0.1 M.

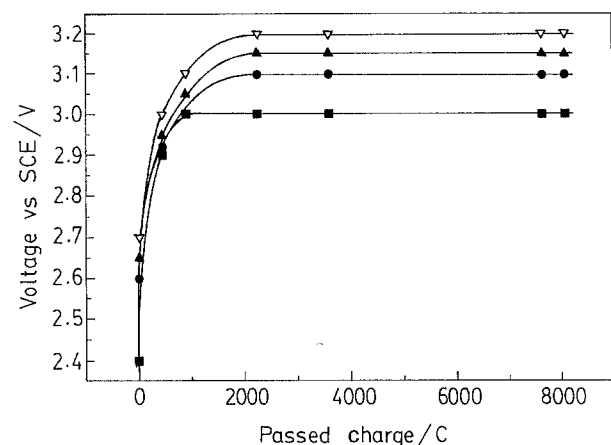


Fig. 9. Dependence of electrolytic voltage against charge passed at various electrodes obtained by the codeposition of PbO_2 microparticles and polypyrrole at different concentrations of pyrrole. Operation conditions: electrode: SPCP; $V = 100$ ml; $T = 25^\circ\text{C}$. Stirring rate: 350 r.p.m.; $i = 0.5$ mA cm^{-2} ; $C_p = 125$ mg dm^{-3} . Key: (∇) 0.01, (\blacktriangle) 0.05, (\bullet) 0.075 and (\blacksquare) 0.1 M.

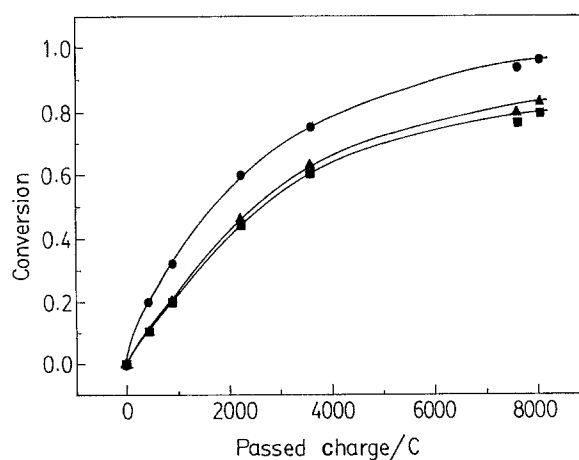


Fig. 10. Plot of the conversion of 2-chlorophenol against charge passed at various electrodes obtained by the codeposition of PbO_2 microparticles and polypyrrole at different voltages. Operation conditions: electrode: SPCP; $V = 100$ ml; $T = 25^\circ\text{C}$. Stirring rate: 350 r.p.m.; $i = 0.5$ mA cm^{-2} ; $C_p = 125$ mg dm^{-3} . Key: (\blacksquare) 1.5, (\bullet) 1.0 and (\blacktriangle) 0.5 V vs SCE.

operated galvanostatically decreases with increase in pyrrole concentration. This indicates that the reaction resistance of codeposition decreases with increasing pyrrole concentration. Consequently, thicker SPCP electrodes were obtained as the concentration of pyrrole increased and more PbO_2 microparticles were incorporated into the SPCP electrodes. The PbO_2 microparticles and polypyrrole are the hydrophilic-active sites and hydrophobic-inactive sites, respectively. The higher the conversion of 2-chlorophenol and the efficiency of oxidation, the more hydrophilic-active sites on the SPCP electrodes occurred. A plot of voltage against charge passed is shown in Fig. 9. This shows that the SPCP electrodes remain stable during the oxidation of 2-chlorophenol. The effects of the SPCP electrodes prepared by the codeposition of PbO_2 microparticles and polypyrrole at different voltages (vs SCE) on the conversion of 2-chlorophenol and the efficiency of oxidation, respectively, are shown in Figs 10 and 11. The dependence of voltage against charge passed at various SPCP

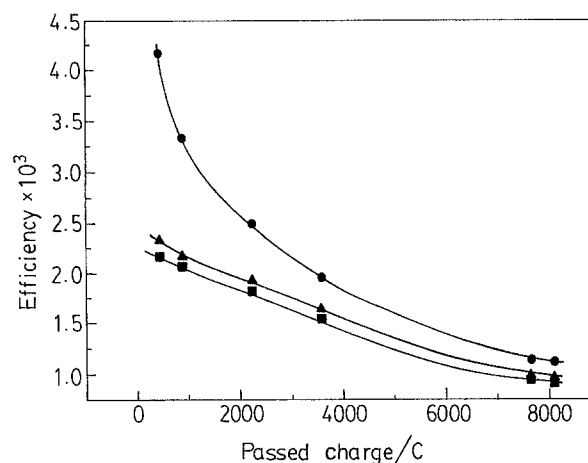


Fig. 11. Plot of the efficiency of oxidation against charge passed at various electrodes obtained by the codeposition of PbO_2 microparticles and polypyrrole at different voltages. Operation conditions: electrode: SPCP; $V = 100$ ml; $T = 25^\circ\text{C}$. Stirring rate: 350 r.p.m.; $i = 0.5$ mA cm^{-2} ; $C_p = 125$ mg dm^{-3} . Key: (\blacksquare) 1.5, (\bullet) 1.0 and (\blacktriangle) 0.5 V vs SCE.

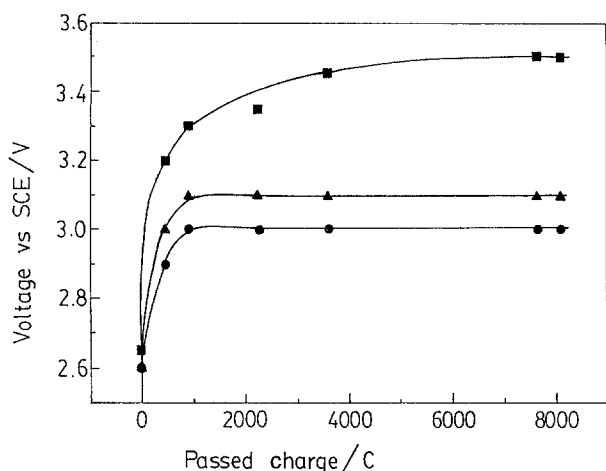


Fig. 12. Dependence of electrolytic voltage against charge passed at various electrodes obtained by the codeposition of PbO_2 microparticles and polypyrrole at different voltages. Operation conditions: electrode: SPCP; $V = 100$ ml; $T = 25^\circ\text{C}$. Stirring rate: 350 r.p.m.; $i = 0.5 \text{ mA cm}^{-2}$; $C_p = 125 \text{ mg dm}^{-3}$. Key: (■) 1.5, (●) 1.0 and (▲) 0.5 V vs SCE.

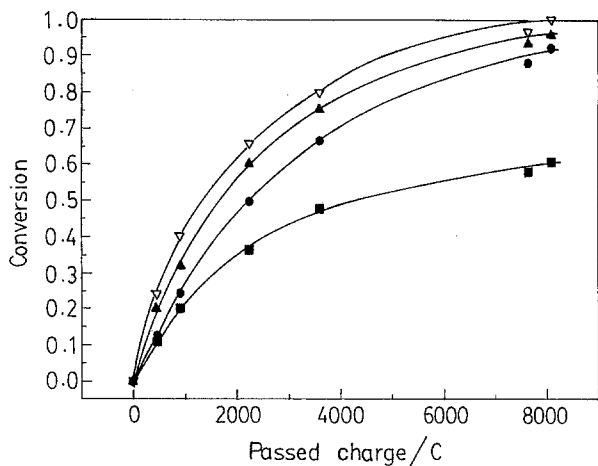


Fig. 13. Plot of the conversion of 2-chlorophenol against charge passed at Pt, SP, and SPCP electrodes. Operation conditions: electrode: $V = 100$ ml; $T = 25^\circ\text{C}$. Stirring rate: 350 r.p.m.; $i = 0.5 \text{ mA cm}^{-2}$; $C_p = 125 \text{ mg dm}^{-3}$. Key: (▽) SPCP-2; (▲) SPCP-1; (●) SP; (■) Pt.

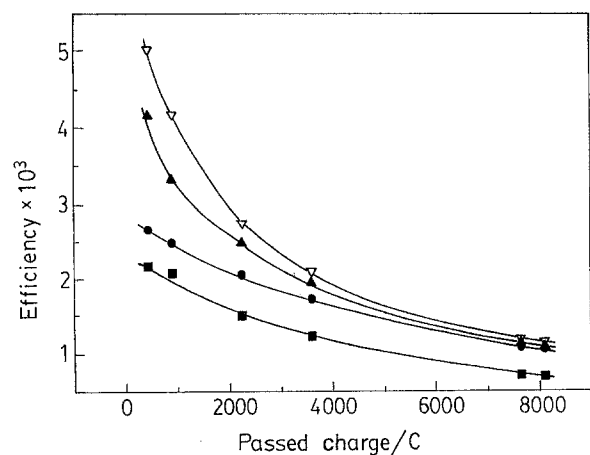


Fig. 14. Plot of the efficiency of oxidation against charge passed at Pt, SP, and SPCP electrodes. Operation conditions: electrode: $V = 100$ ml; $T = 25^\circ\text{C}$. Stirring rate: 350 r.p.m.; $i = 0.5 \text{ mA cm}^{-2}$; $C_p = 125 \text{ mg dm}^{-3}$. Key: (▽) SPCP-2; (▲) SPCP-1; (●) SP; (■) Pt.

electrodes is demonstrated in Fig. 12. The optimum conversion of 2-chlorophenol and the efficiency of oxidation were obtained when the SPCP electrode was prepared at 1.0 V vs SCE. The reason for the lower conversion and efficiency on the SPCP electrode obtained at 1.5 V vs SCE than those at 1.0 V vs SCE is probably due to the degradation of polypyrrole on the SPCP electrode prepared at a potential which is too high [17]. On the other hand, the thickness of the SPCP electrodes obtained at 0.5 V vs SCE was smaller than that at 1.0 V vs SCE. This smaller thickness reduced the number of active sites (PbO_2) and lowered the conversion of 2-chlorophenol and the efficiency of oxidation.

3.5. Electrooxidation of 2-chlorophenol at different electrodes

The electrocatalytic oxidation of 2-chlorophenol was carried out galvanostatically on the Pt, SP, and SPCP electrodes. The results are shown in Figs 13 and 14. The conversion of 2-chlorophenol and the efficiency of oxidation on the SP electrode are larger than those on the Pt electrode, owing to its higher oxygen overpotential [18]. Oxygen evolution was inhibited but the efficiency of oxidation of 2-chlorophenol was enhanced on the SP electrode. The conversion of 2-chlorophenol and the efficiency of oxidation were improved by the hydrophobic-modified SPCP electrode. The hydrophobicity of the SPCP electrode is better than that of the SP electrode. It is apparent that the electrolysis of the organic substrates (2-chlorophenol) on the hydrophobic-modified SPCP electrode is more strongly promoted than on the SP electrode due to strong hydrophobic interaction between the hydrophobic electrode surface and the hydrophobic organic substrates [16].

4. Conclusion

The electrocatalytic oxidation of 2-chlorophenol on a composite PbO_2 /polypyrrole electrode was examined. The composite PbO_2 /polypyrrole electrode was obtained by the codeposition of PbO_2 microparticles and polypyrrole. The electrocatalytic oxidation of 2-chlorophenol was enhanced on the hydrophobic-modified PbO_2 /polypyrrole anode due to the reactant concentrated effect. The efficiencies of the 2-chlorophenol oxidation on these electrodes were found to lie in the order: composite PbO_2 /polypyrrole electrode > PbO_2 electrode > Pt electrode. The thicker the composite (PbO_2 /PPy) layer, the more active-sites in the composite electrode and the more 2-chlorophenol could be oxidized. The electrocatalytic oxidation of 2-chlorophenol was improved on the PbO_2 electrode due to the high oxygen overpotential of PbO_2 . The electrocatalytic oxidation of the hydrophobic organic reactant was strongly enhanced on hydrophobic-modified electrodes due to strong hydrophobic interaction between the hydrophobic electrode surface and the hydrophobic organic substrates.

Acknowledgements

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