

Auto-inhibition effects in anodic oxidation of phenols for electrochemical waste-water purification*

H. AL-MAZNAI and B. E. CONWAY

Department of Chemistry, University of Ottawa, 10 Marie Curie Street, Ottawa, ON. K1N 6N5 Canada

(Received 27 August 2001)

Removal or modification of noxious organic impurities in waste-waters is a major challenge for environmental science. Pollutants such as phenols and their derivatives, as well as PCBs, have attracted special attention. In recent years, the possibilities of effecting direct electrocatalytic oxidations at high-area electrodes such as supported Pt or RuO₂ have been investigated. However, in a number of cases, especially with phenolic impurities, application of anodic oxidation fails to lead to continuous Faradaic oxidation currents owing to the electrode surfaces becoming blocked with polymeric oxidation products leading to auto-inhibition ("passivation") of the desired electrode process. Examples of such effects with phenols and related compounds are examined comparatively in the present paper by means of cyclic voltammetry and chronoamperometry.

Keywords: phenol, waste-water purification, electro-oxidation, auto-inhibition.

1. INTRODUCTION

Electrochemical processes offer useful possibilities for *in situ* and local treatment of industrial waste-waters, either at cathodes for removal of traces of heavy metal ions or complexes, or at anodes for destructive removal or modification of noxious solutes (especially organics). For the latter type of impurity solutes, the overall process most desirable is that of so-called "mineralization", *i.e.*, complete anodic oxidation to CO₂ and H₂O, or additionally to N₂ or NO₃⁻, or to SO₄²⁻ in the case of N or S containing organics, respectively.

Treatment of industrial waste-waters for removal of inorganic or organic impurities has been a long-standing aspect of environmental science and technology. Filtration procedures using various high-area adsorbents have formed the basis of large-scale water purification technologies. However, in recent years, the possibility of employing more substance-specific and more sophisticated procedures such as *in situ* photo-catalytic and direct electrochemical oxidation or reduction processes for impurity removal or modification to

* Dedicated to Professor Dragutin M. Dražić on the occasion of his 70th birthday.

less noxious products have been envisaged and experimentally realized. Several important review publications on these approaches have appeared.^{1,2}

Direct adsorption of organic impurities in waste-waters on high-area granular charcoal has been a common procedure for removal of dissolved, noxious compounds in provision of municipal drinking waters. However, such a process, operated on a large practical scale, is expensive and requires an operable regeneration process. One such approach is thermal treatment at elevated temperatures which, however, can be expensive. Electrochemical reactivation has been proposed and demonstrated; however, with phenols, this process is ineffective owing to irreversibility and incompleteness in the electrocatalytic oxidation of such adsorbates. This is the subject of the present paper.

The possible use of electrochemical Faradaic oxidation as a process for waste-water purification has been reviewed in a conference proceedings volume¹ and in a recent comprehensive monograph² which also treats other methodologies such as photo-catalytic oxidation in a quasi-3-dimensional system employing suspended TiO₂ particles. On the other hand, use of electrode processes has the advantage that no added oxidizing or reducing agent needs to be provided since electrons (at cathodes) or their vacancy states (at anodes) are direct reagents, so that no other undesired exogenous products will arise.

The electrochemical methodologies employ procedures such as: a) reduction at high-area substrate electrodes such as porous C materials, or porous or mesh metal electrodes at which metal ions can be removed by Faradaic deposition; b) anodic oxidation at similar high-area electrode modules,³ especially consisting of anode materials at which electrocatalytic oxidations of organics can take place; and c) production *in situ* of some solution-soluble oxidizing reagent by means of an electrolytic Faradaic reaction, *e.g.*, formation of hypochlorite, hydrogen peroxide, persulfate or ozone.

Procedures a) and b) have the advantage that electrons themselves (as at cathodes), or electron-vacancy states (as at anodes) are the reagents for the purification process, although a conducting solution must be involved. Various examples of application of such procedures are to be found in the literature, *e.g.* in Refs. 1 to 6. Electrochemical procedures also have the advantage that they can be set up locally, on site, at or near to the industrial source of the pollution.

Since quite low levels of impurities are still environmentally significant, electrochemical procedures will usually be under diffusion-control so that large specific-area materials are required¹ for the electrodes and mechanically assisted mass-transport of the dissolved impurities should be provided, *e.g.*, employing flow-through or flow-past porous electrode configurations, or rotating-mesh vane electrodes.^{1,3} By such means the regular 2-dimensionality of most electrode configurations can be replaced by quasi-3-dimensionality³ leading to minimization of diffusion-control which otherwise dominates the kinetics of electrode processes at a planar electrode in sufficiently dilute solutions of an electro-active reagent.

Electro-oxidation or reduction processes have, however, a common limitation; this is because electrode processes are normally two-dimensional, involving electron

transfer (and other coupled reactions) that requires a metal or metal oxide (*e.g.*, oxidized Pt, SnO₂ or RuO₂⁴⁻⁶) surface on which to take place. This limitation can be attenuated by conducting the electrochemistry in a quasi-3-dimensional way^{3,4} at high specific area materials such as porous carbon, carbon cloth or at sintered metal powder electrodes. This tends to eliminate or minimize diffusion control in the desired electrode process which otherwise arises due to the normally low-concentration conditions which commonly obtain in impurity-containing waste-waters.

The processes of anodic removal of trace organics at anodes have much in common with fuel-cell anode reactions. Such processes involve the coupling between electrosorption or dissociative electrosorption and electrocatalytic reaction processes.^{7,8} The simplest example is the electro-oxidation of H₂ to hydrated H⁺ or H₂O. However, for even simple organics, such as HCOOH or CH₃OH, electro-oxidation usually involves self-inhibition processes due, in those cases, to parallel formation of CO which is strongly adsorbed.³

Amongst the variety of noxious compounds commonly present in industrial waste-waters (depending on processes being operated) are phenols^{1,4-6} and from various sources, PCB's, having structures related to phenols. Despite the importance of developing processes for removal or structural modification of phenols, rather few direct studies on electrochemical reactivity of phenols have been reported in the literature, but Refs. 3-5 and 6 are significant examples. The ideal requirement is so-called complete "mineralization", *i.e.*, oxidation to CO₂ and H₂O (or OH⁻), as mentioned above, but such complete electrochemical degradation is rare except with short-chain alcohols, aldehydes or substances such as N₂H₄ or NH₃. However, an early paper¹⁰ reports a study of oxidation of toluene to CO₂ and H₂O at PbO₂ electrodes, but this conversion is inefficient with only low yields.

In the case of phenol, electro-oxidation, *e.g.*, at Pt anodes, becomes easily self-inhibited due to anodic polymerization,^{6,7} leading to "passivation" of the Pt surface. Phenomenologically, this passivation is similar to that observed at metals such as Fe or Ni, extensively studied by Professor Dražić, but the surface chemistry involved is, of course, quite different, being involved with oxide-film formation, *e.g.*, in the cases of Fe or Ni. The present paper examines the self-inhibition in phenol oxidation by means of linear-sweep voltammetry and chronoamperometry⁹ at Pt electrodes in aqueous solution, bearing surface-oxide films formed under various conditions of anodization.

Direct electrochemical adsorption and regeneration has been studied with several adsorbates, *e.g.*, ethyl xanthate, at high-area carbon cloth electrodes by Ayranci and Conway¹¹ where it was demonstrated that reversal of polarity of polarized high-area C electrodes could lead to almost quantitative desorption of the adsorbate after periods of *ca.* 30 min or more. Under such conditions, however, the adsorption is largely physical and electrostatic (in the double-layer of the C electrode), unlike, *e.g.*, the case of adsorption of phenols at Pt electrodes.^{1,6} At carbonaceous materials, the adsorption is not only dependent on the available real surface area, but on the provenance of the C material, its pretreatment and the pore-size distribution, especially that of the finest pores almost of molecular dimensions.

In the case of phenol, Coughlin and Ezra¹² demonstrated that extensive surface oxidation of activated carbon leads to appreciable decreases in its adsorbability for phenol, nitrobenzene and benzene sulfonate. Thus, oxidation of activated C by aqueous Cl₂ (ClO⁻) was found to increase the surface functionality by O-containing groups (-COOH, >CO) which decreased the adsorption capacity for phenol.¹³

More relevant to the present topic of inhibition of adsorption of phenol at Pt by anodic oxidation is the observation¹⁴ that adsorbed molecular O₂ causes changes in the adsorbability at granular activated C for phenol and nitrobenzene due to an appreciable uptake of O₂ (10 to 40 mg g⁻¹, Ref. 15). Vidic *et al.*¹⁶ found that the presence of molecular O₂ at activated C actually had the effect of increasing its adsorption capacity up to 3-fold for adsorbates such as phenol, *o*-cresol and 3-ethyl phenol. This effect was attributed to polymerization of the phenols on account of the free radical character of O₂, allowing more extensive uptake of the phenols. However, the resulting enhanced adsorption was presumably irreversible and later Vidic *et al.*¹⁷ found that O₂ had little effect on the adsorption of nitrophenols at C.

2. EXPERIMENTAL

2.1. Procedures employed

For the principal purpose of the work, cyclic voltammetry and chronoamperometry procedures were employed. These provided, respectively: a) the potential ranges over which the selected phenolic compounds, listed in Section (2.2) showed oxidative electrochemical reactivity at the Pt electrode, and b) the time-dependence of rates of such oxidation processes at several controlled electrode potentials. In some experiments, reactivity behaviour was followed over a range of temperatures from 293 to 343 K.

In the voltammetry experiments, the extents to which the anodic oxidative response currents declined (auto-inhibition effect) over the first several cycles were easily observable and were recorded and compared for the series of the several phenolic compounds investigated, including chlorophenols.

In several specially designed experiments, an anodic oxide film was first grown at Pt at a controlled, relatively high positive potential¹⁸ for a controlled period of time (*cf.* Ref. 17), and then allowed to come into contact with a dilute phenol solution. The purpose was to see if phenol could be oxidized by such a film at 2.2 V *vs.* Pd/H on open-circuit, as is known for the case of oxidation of HCOOH by such Pt surface oxide films. In some related experiments, the extent of oxidative loss of phenol by electrochemical oxidation was followed by means of UV spectrophotometry. However, although oxidation takes place initially in a single current peak in the cyclic voltammograms (see below), it is not sufficient to be analytically detected by spectrometry.

2.2. Adsorbate compounds

The following phenolic-type and related compounds were studied as adsorbates at polycrystalline Pt: i) phenol itself (Aldrich, 99 %); ii) 2-chloro- and 4-chlorophenols (Aldrich, 99 %); iii) 2,6-dichlorophenol (Aldrich, 99 %); iv) catechol (Aldrich, 99 %); v) hydroquinone and 1,4-benzoquinone (Aldrich, 98+ %). Each of these compounds was made up in high-purity H₂SO₄ or NaOH solutions at relatively low concentrations of 0.01, 0.1 or 0.05 M of the adsorbates. Comparative electrosorption experiments at Pt were conducted also with pyridine and ethyl xanthate, which will be reported elsewhere.

2.3. Supporting electrolyte solutions

Experiments were conducted in aqueous H₂SO₄ (Aldrich, 99.9 % purity) and NaOH (BDH, Aristar grade) solutions prepared from the respective high-purity reagents in 18 Mohm-cm Milli-Q high-purity water (*cf.* Ref. 19).

2.4. Pt and other electrodes

Platinum gauze electrodes, made from high-purity Pt wire, were sealed to short lengths of pure, pre-cleaned, Pt wires, the latter being sealed, leak-free, in a glass-tube electrode holder. Before use in an experiment the platinum electrode was flame annealed in the flame of an oxy-gas torch. Counter electrodes were prepared similarly. A Pd/H electrode was used as a reference element to avoid bubbling of H₂ in the cell reference-electrode compartment from which traces of dissolved H₂ can become transferred to the working electrode despite use of a closed, wetted stopcock, in the usual way. This procedure avoids any spurious currents due to oxidation of traces of H₂.

The initial cleanliness (*cf.* Ref. 20) of the Pt working electrode was checked by comparison of voltammograms initially recorded in the additive-free aqueous H₂SO₄ or NaOH supporting electrolytes in comparison with the voltammograms for polycrystalline Pt previously obtained²⁰ under rigorously clean conditions for preparation of electrode surfaces, solutions and cells. The voltammetric signatures obtained at Pt in the present work were virtually identical with those published previously.^{19,20}

2.5. Cyclic voltammetry and chronoamperometry

Cyclic voltammetry experiments were conducted in the usual way using instrumentation based on a Princeton Applied Research Model 173 potentiostat/galvanostat and a Nicolet 310 digital oscilloscope coupled with an Hokuto Denko HB-104 function generator capable of applying linear potential scans to the potentiostat, functioning as a potentiodyne, at various voltage sweep-rates.

Chronoamperometry was conducted with the same equipment, but with the function generator providing fast step-changes of applied potential. Current *vs.* time transients were analysed by means of an equation (see Section 3.2.1.) taking into account build-up of an inhibiting intermediate species. All current-response behaviours in cyclic voltammetry and chronoamperometry were recorded on the Nicolet 310 digital oscilloscope and then digitally processed from diskettes on a PC.

In the voltammetry experiments, special attention was given to the extent(s) to which the electrochemical oxidation response-current profiles became self-inhibited as soon as the Pt electrode surface was exposed to the phenolic compounds. Usually self-inhibition was almost complete over *one* cycle with phenol itself or over only *a few* cycles up to 1.1 to 1.4 V (RHE) with the other compounds, except the quinones.

In the chronoamperometry experiments, anodic response-current transients were followed in time up to *ca.* 800 s, after stepping the potential of the Pt electrode positively and successively to a series of increasing potentials from *ca.* 0.5 V to 1.5 V (RHE). The fall-off of the response-current was usually 90 % completed in the first few seconds, up to 10 s. Analysis of the transients in time (*t*) was made by means of $\ln i(t)$ *vs.* time plots (see below).

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry behaviour of phenols at polycrystalline Pt electrodes

3.1.1. Phenol, catechol and hydroquinone

Figures 1a, b and c show the CVs for oxidation of phenol at 0.01 M concentration at polycrystalline Pt in 1.0 M aq. H₂SO₄ at 293 K plotted on a potential scale *vs.* the Pd/H reversible electrode. The sweep-rates are respectively 5, 50 and 100 mV s⁻¹ for the three curves. First-cycle oxidation currents are detectable (beyond the double-layer charging current) at *ca.* 0.9 V and lead to a well defined anodic current peak centered at potentials in the range 1.13, 1.23 and 1.25 V, with increasing sweep-rate in the range stated above. The currents beyond those for the peak, when observed, appear to be continuing currents for surface oxidation of the Pt,^{21,22} but become progressively overlaid by the current responses for phenol oxidation as the positive going sweep-rate is increased (Fig. 1c).

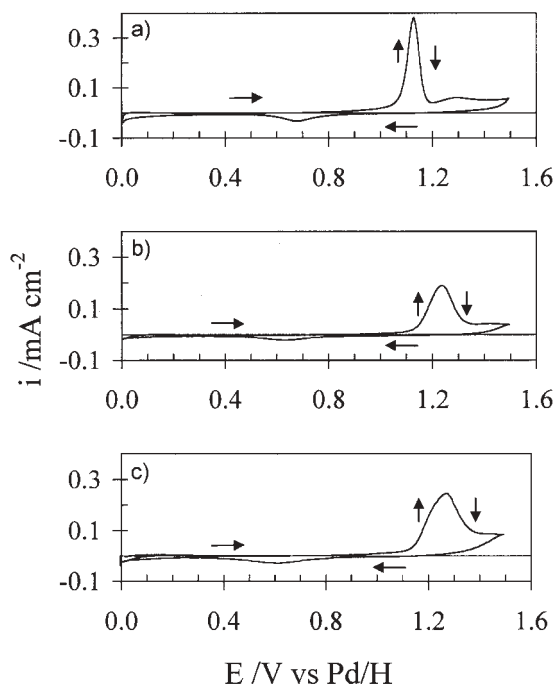


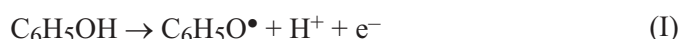
Fig. 1. First cycle cyclic voltammogram for the electro-oxidation of 0.01 M phenol in 1.0 M aq. H_2SO_4 at a Pt gauze electrode at scan rates of a) 5 mV s^{-1} , b) 50 mV s^{-1} and c) 100 mV s^{-1} .

The charge for the main peak, which must be associated with phenol oxidation, is $10.6 \pm 0.05 \text{ mC cm}^{-2}$ which diminishes somewhat with increasing sweep-rate. However, the rise and the form of the anodic current peak profile is unaltered with stirring so is not diffusion controlled. It is presumably due to oxidation of phenol in the adsorbed state.

Two important features of the voltammograms of Figs. 1a, b and c are: a) that no reduction-current peak arises on the negative-going sweep, conjugate to the large anodic peak, so that the latter corresponds to a totally irreversible process. b) Secondly, on the second and subsequent sweeps, *no* response current peak arises that could correspond to continuing or repeated oxidation of phenol. This is, of course, due to the observed absence of any process of reduction of the inhibiting species formed in the anodic peak. Also, no continuous Faradaic currents pass at any potential in the range 0.1 to 1.5 V (Pd/H), so any continuing oxidation of phenol is completely inhibited by the species formed in the peak at 1.13 V. However, a residual-current peak is observable in negative-going sweeps (owing to the scale required to show the anodic peak, this reduction peak appears small in Fig. 1) over the range 0.85 to 0.55 V (Pd/H) which corresponds to the potential range where reduction of anodically formed Pt surface-oxide species normally takes place²⁰ in the absence of any other adsorbate. However, the charge for that peak, seen after oxidation of the phenol, is significant, *viz* $-1.90 \pm 0.05 \text{ mC cm}^{-2}$ and is hence to be attributed to reduction of residual oxide following formation of adsorbed phenol species in the main anodic peak. Note that this cathodic peak corresponds to substantially less charge than that

passed anodically *beyond ca. 1.2 V* up to 1.5 V in the voltammogram of Fig. 1a, *i.e.*, after the process corresponding to the main peak has been completed. Similar behaviour is seen in Figs. 1b and c at higher sweep-rates.

Since the charge corresponding to the main peak is much more than that for monolayer electrosorption, the results suggest that anodic polymerization of phenol takes place, leading to a multilayer film. The primary step (I) is a $1e^-$ oxidation:²⁴



leading to the indicated phenoxy radical which can then undergo dimerization or polymerization with other phenol molecules to form a polyphenylene oxide. Oxidative polymerization of phenolic compounds is well known.

The same kind of anodic behaviour occurs at Pt in alkaline solution (Fig. 2) where the reagent is the phenolate anion. However, in this case under alkaline conditions, the electrode is not passivated immediately on the first cycle but requires four or five anodic/cathodic cycles for complete inhibition to set in (Fig. 2). This is consistent with the anion being less easily oxidizable due to its stabilization by hydration in solution (*cf.* Ref. 25).

The behaviour of benzoquinone was also examined comparatively (Fig. 3). As expected from the known reversibility of the benzoquinone/hydroquinone couple, cyclic voltammetry of benzoquinone showed reversible reduction/reoxidation within the potential range 1.0 to 0.3 V (Pd/H) without inhibition effects setting in, indicating absence of electrochemical polymerization. However, this is because the redox reaction between quinone/hydroquinone functions is involved in the case of benzoquinone. Thus, no irreversible

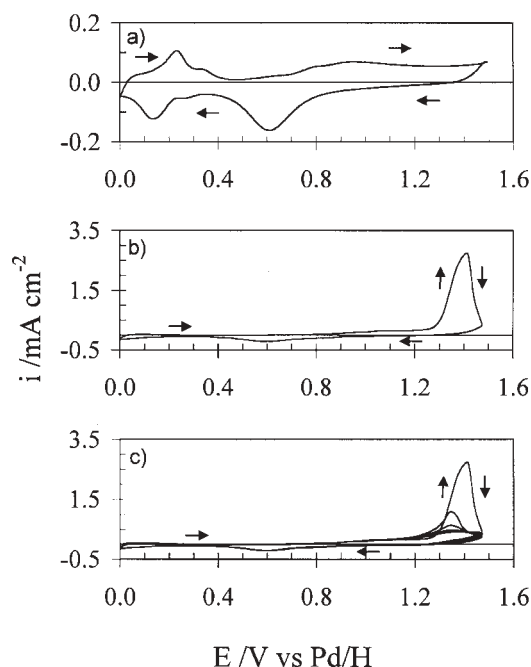


Fig. 2. Cyclic voltammograms at a Pt gauze electrode at a scan rate of 50 mV s^{-1} in: a) 1.0 M NaOH, b) first cycle CV of the electro-oxidation of 0.01 M phenol and c) as in b) but with continuous cycling.

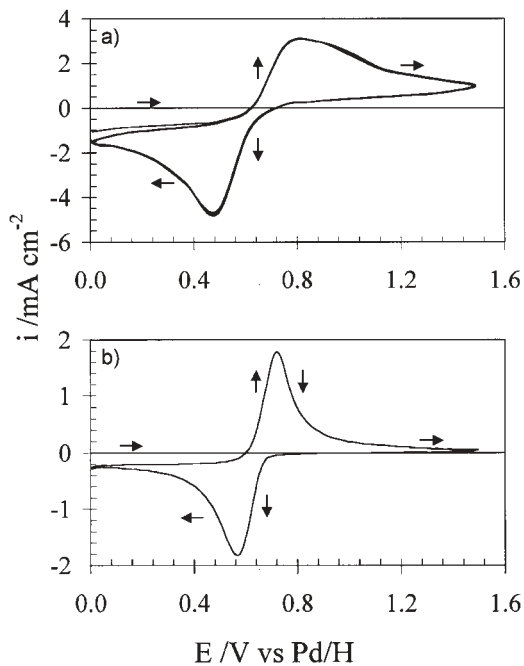


Fig. 3. E - i profiles for the electro-oxidation of 0.01 M 1,4-benzoquinone in 1.0 M aq. H_2SO_4 at a Pt gauze electrode at scan rates of a) 50 mV s^{-1} and b) 5 mV s^{-1} .

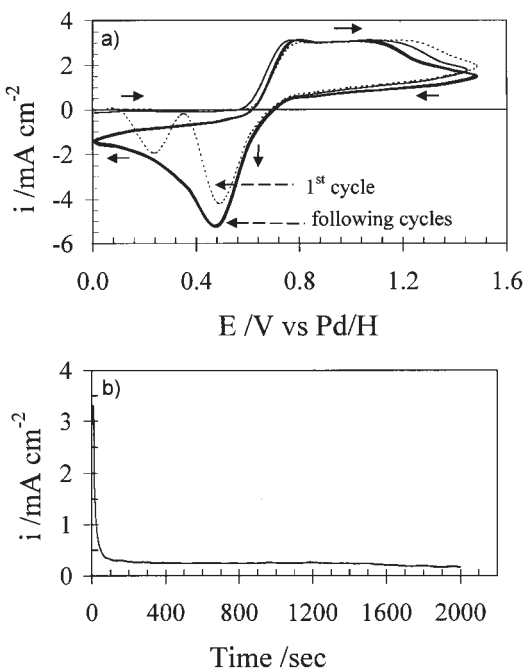


Fig. 4. Electro-oxidation voltammograms for 0.01 M hydroquinone in 1.0 M aq. H_2SO_4 at a Pt gauze electrode a) E - i profiles at a scan rate of 50 mV s^{-1} and b) the current-time profile.

anodic current peak arose over the whole scanned potential range, *i.e.*, up to 1.5 V. The form of the anodic and cathodic half-cycle curves correspond to those for diffusion control.

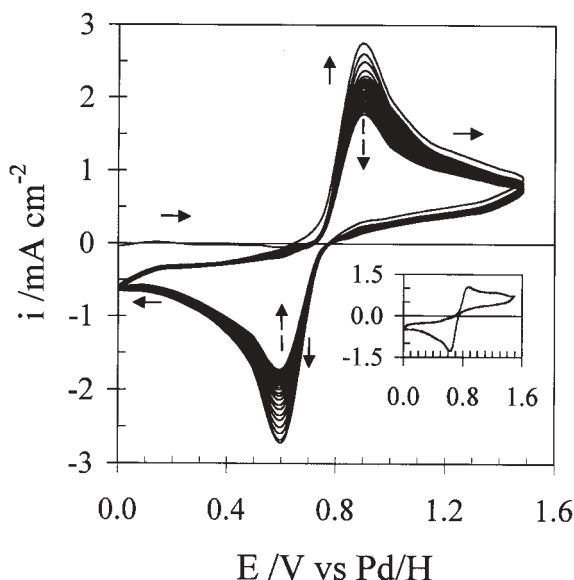


Fig. 5. E - i profiles for the electro-oxidation of 0.01 M catechol in 1.0 M aq. H_2SO_4 at a Pt gauze electrode at a scan rate of 50 mV s^{-1} . Inset shows cyclic voltammogram for final cycle no. 30.

Starting with hydroquinone as the reagent gave similar behaviour (Fig. 4), the system can be multiply cycled. Oxidation currents pass over a broad potential range from 0.6 to ca. 1.3 V (Pd/H) and a reduction peak arises on negative-going scans, commencing at 0.68 V. However, the system is kinetically irreversible, but the anodic and cathodic current profiles cross the zero-current line at the same potential region, 0.6 to 0.7 V (Pd/H) as that for benzoquinone (Fig. 3).

Figure 5 shows the cyclic voltammetry behaviour of catechol (*o*-hydroxyphenol) in 1.0 M aq. H_2SO_4 ; it is very different from that of phenol and can be cycled reversibly over many anodic/cathodic current cycles centered around a potential of 0.75 V (Pd/H). However, eventually, with continued cycling, both the anodic and cathodic peak currents tend to diminish but even after 90 min cycling appreciable activity remains (see inset in Fig. 5). The behaviour suggests formation and reduction of *ortho*-quinone; no irreversible formation of a blocking polymer is indicated except, perhaps to a small extent accounting for the slow deactivation of the Pt surface. Note that the forms of the anodic/cathodic current profiles are similar to those for a diffusion-controlled reversible process involving presumably here the *o*-hydroquinone (catechol) and *o*-benzoquinone couple. No further degradative oxidation is indicated.

3.1.2. Substituent effects with chlorophenols

The voltammetric behaviours of 2-chloro-, 4-chloro- and 2,6-dichlorophenols at Pt were examined and are illustrated comparatively in Figs. 6, 7 and 8. The voltammograms are for a scan rate of 50 mV s^{-1} at a concentration of 0.1 M. Cl-substitution in the phenol structure tends to increase the acidity of the phenolic OH groups.

2-Chlorophenol behaves like phenol itself, exhibiting a well-defined and almost symmetrical single anodic current peak centered at 1.13 V (Pd/H) and corresponding to

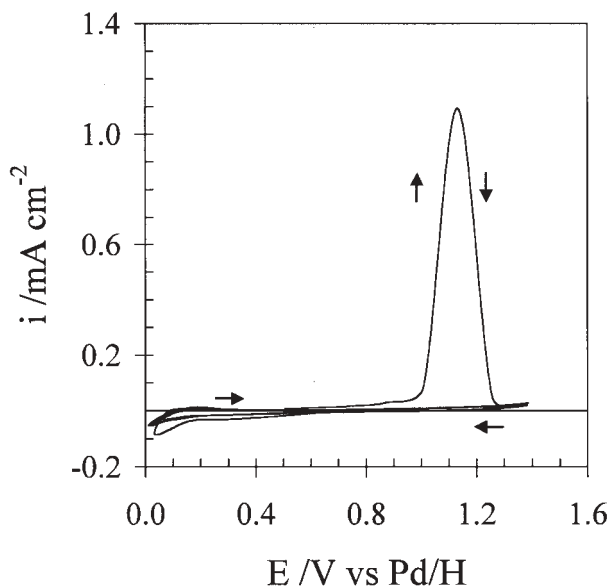


Fig. 6. E - i profiles of the electro-oxidation of 0.1 M 2-chlorophenol in 0.1 M aq. H_2SO_4 at a Pt gauze electrode at a scan rate of 50 mV s^{-1} .

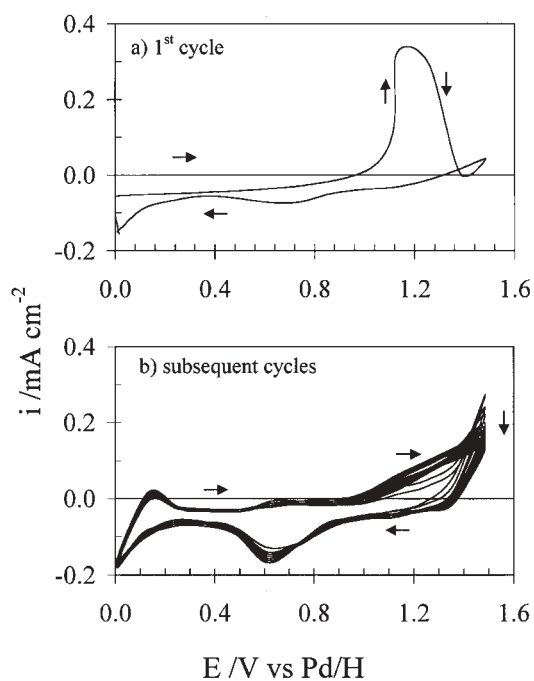


Fig. 7. E - i profiles of the electro-oxidation of 0.01 M 4-chlorophenol in 1.0 M aq. H_2SO_4 at a Pt gauze electrode at a scan rate of 50 mV s^{-1} : a) first cycle and b) following cycles. (Current arise below the zero-current line due to O_2 evolution beyond ca. 1.35 V).

passage of $1.90 \pm 0.05 \text{ mC cm}^{-2}$ of charge. Note, in contrast to the CV for phenol (Fig. 1), no following oxidation current peak(s) arise, corresponding to possible residual surface oxidation of the Pt substrate, nor does any current peak arise on the negative-going

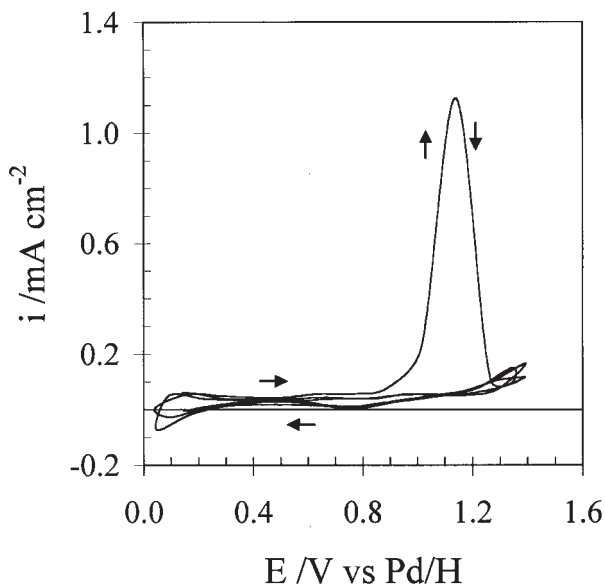


Fig. 8. $E-i$ profiles of the electro-oxidation of 0.1 M 2,6-dichlorophenol in 0.1 M aq. H_2SO_4 at a Pt gauze electrode at a scan rate of 50 mV s^{-1} .

sweep around 0.5 to 0.7 V which would correspond to reduction of residual surface oxide on Pt (*cf.* Fig. 1 again) or of the polymeric film. After passage of anodic charge in the single peak, the electrode remains completely deactivated and no residual currents pass.

The anodic peak, as for the case of phenol itself, must be attributed to formation of a completely inhibiting polymer film. For a $1e^-$ formation of a radical per Pt site, the above charge would correspond to formation of a film about 9 equivalent monolayers in thickness.

4-Chlorophenol also exhibits a single but broader anodic current peak between 1.0 and 1.4 V (Pd/H) followed by almost complete deactivation of the Pt surface in subsequent cycling.

2,6-Dichlorophenol again shows a well developed single anodic peak (Fig. 8) arising between 0.95 and 1.29 V, centered at *ca.* 1.12 V (Pd/H), also with almost no further current response up to 1.4 V and correspondingly, with no development of a cathodic current response in the oxide reduction region of Pt. Thus, the activity of the electrode is again completely suppressed by the polymeric species (formed in the main peak) which is evidently non-reducible, as for the case of phenol itself. The charge under the single peak in Fig. 8 is $2.63 \pm 0.05 \text{ mC cm}^{-2}$, again corresponding to multilayer formation of an inhibiting polymeric product.

The case of catechol can be regarded as an *ortho*-substituted phenol, but behaving as a redox system like hydroquinone/benzoquinone, catechol being the reduced form of *o*-quinone. Thus, its cyclic voltammogram is like that for benzoquinone (Fig. 3), and no inhibiting behaviour arises, even on multiple cycling; nor are there indications of anodic degradation. The voltammograms of Fig. 5 exhibit only gradual inhibiting behaviour but are

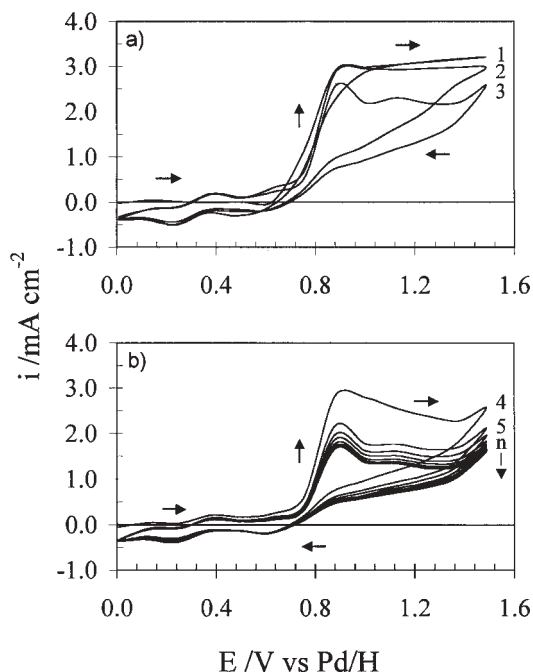


Fig. 9. Electro-oxidation voltammograms of 0.01 M catechol in 1.0 M aq. NaOH at a Pt gauze electrode at a scan rate of 50 mV s^{-1} : a) first 3-cycles and b) subsequent cycles.

not influenced by stirring. The *o*-hydroquinone/quinone reversible redox couple evidently acts as a “protective” function with respect to further oxidation involving polymerization.

In 1.0 M aq. NaOH solution (Fig. 9), the voltammetry behaviour of catechol (0.01 M) is quite opposite from that in acidic solution. Anodic oxidation current profiles commence at *ca.* 0.75 V (Pd/H), as in acidic solution, but appreciable anodic currents extend over a broad region to 1.5 V. On sweep-reversal, anodic currents are maintained on the negative-going sweep, but at lower values, until they diminish to zero at *ca.* 0.7 V. However, no appreciable reduction current peaks arise on cycling as they do for catechol in acidic solution (Fig. 5). Also, the anodic currents progressively diminish with repeated cycling, as indicated in Fig. 9b, but again no sharp anodic peak, leading to inhibition, arises as it does characteristically for oxidation of phenol or Cl-substituted phenols at Pt (Figs. 1 and 6).

3.2. Chronoamperometry results

3.2.1. General transient behaviour

Chronoamperometry experiments were conducted in order to examine the time-dependence of anodic oxidation of phenol and its related derivatives at Pt. Amongst other purposes, this procedure was adopted for the practical aim of examining conditions under which a continuous current for phenol oxidation, and possible destruction, might be realized. A series of potentiostatic potential steps were successively applied to the Pt electrode, progressively increasing its potential to higher positive values up to 1.5 V (Pd/H). The resulting anodic current transients were recorded on the digital oscilloscope over times up to 800 s or more.

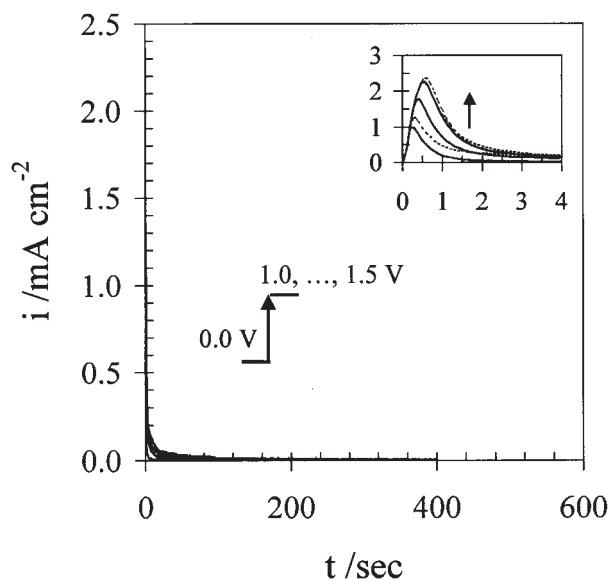


Fig. 10. Chronoamperometric current-time transients for oxidation of 0.05 M phenol in 0.5 M aq. H_2SO_4 at a Pt gauze electrode at a "70" sonicator voltage.

The transients were of the expected general form with an initial rapid rise of current for double-layer charging followed by decline of currents over an extended period of time, but with most of the decline, *ca.* 90 %, being completed in about 5 to 10 s. The transients never attained steady net anodic currents owing to the persistence of the inhibition effects found in the cyclic voltammetric experiments. Some examples are shown in the Figures which follow.

Figure 10 shows a series of chronoamperometric transients for oxidation in 0.05 M phenol in 0.5 M aq. H_2SO_4 at 293 K under sonication. Positive-going potential steps were from 0.0 V (Pd/H) to 1.55 V, down to 0.5 V, *i.e.*, over the potential range in which the main anodic current peak arises in cyclic voltammetry (Fig. 1a). The transients to the higher potentials seem to attain constant current plateaux for several seconds before onset of declines of current. This suggests that, for a short period of time, a continuous current for phenol oxidation can arise before nucleation and growth of an inhibiting film sets in. This feature is not seen on the insensitive scale of 800 s for the overall transients, extended over a long period (Fig. 10).

For a process in which an inhibiting species is generated that occupies some coverage fraction θ of the electrochemically active surface, the transient current at constant potential, V , is given by

$$i_v = k_v (1 - \theta_v) c \quad (1)$$

where k_v is an experimental electrochemical rate constant for potential V , θ_v is the time(t)-dependent coverage of the inhibiting species and c is the concentration of the reagent (here phenol or other derivatives) that can be oxidized. The time-dependent coverage, θ_v , can be written in terms of the charge $\int i_v dt$ for the Faradaic

generation of the intermediate (here a polymerized form of phenol). θ_v would be the ratio $\int i_v dt / Q_1$ where Q_1 is the charge for full coverage. Then Eq. (1) will read

$$i_v = k_v \left(1 - \frac{\int i_v dt}{Q_1} \right) c \quad (2)$$

which, upon differentiation, rearrangement and re-integration becomes

$$\ln i_v(t) = - \frac{k_v c}{Q_1} t + k \quad (3)$$

where k is an integration constant. Hence $\ln i_v(t)$ should plot out linearly with t for increase of θ below the full coverage limit (see below). This is tested for several transients for phenol oxidation in Fig. 11.

Equation (1) ideally applies to fractional coverages built up to a monolayer limit. However, we have seen that in the voltammetry experiments, the inhibitor species builds up to a multilayer with formation charges of *ca.* $10.60 \pm 0.05 \text{ mC cm}^{-2}$. Similar magnitudes of the formation charge arise from the transients shown in Fig. 10 for phenol. Hence, it must be concluded that the developing inhibitor film does not first form a complete monolayer, but becomes progressively extended sideways and upwards from nuclei on the Pt surface until the film eventually fully blocks the surface with a multilayer film. Some analogy can be drawn here to the mechanism of electrocrystallization of metals^{25,26} where growing discs, hemispheres or cones eventually overlap (model of Avrami²⁷) and lead to blocking of the primary steps of ion deposition on the actual metal surface. The Q in Eq. (1) can be greater than the value appropriate for θ_v for monolayer coverage.

Tests of the time-dependence of the response currents for potentiostatic film growth at Pt in the presence of phenol are shown in Fig. 11, mentioned earlier, plotted according to Eq. (3), originating from Eq. (1). The chronoamperometric transient for oxidation of phenol in 1.0 M aq. NaOH is shown in Fig. 12a and its corresponding plot in $\ln i_v$ vs. t is shown in Fig. 12b. For this case, a finite residual anodic current of *ca.* 0.2 mA cm^{-2} continues to pass for 8000 s or more (Fig. 12a) without decline, although it is much smaller than the maximum current attained (*ca.* 2.45 mA cm^{-2}) at the turning point.

The chronoamperometric transient for catechol oxidation (Fig. 13) is quite different in shape and the current declines to a limit at *ca.* 0.5 s. The difference in behaviour from that observed with phenol or phenolate corresponds to the qualitatively different voltammograms for catechol compared with those for phenol (Fig. 5 vs. Fig. 1a), owing to the involvement of the reversible redox couple that arises in the case of catechol, as noted earlier.

The transients for oxidation of 4-chlorophenol (0.1 M in 0.1 M aq. H_2SO_4) are shown in Fig. 14 for a range of temperatures from 20 °C to 70 °C. In these cases, all transients decline to finite, temperature-dependent, limiting anodic currents beyond *ca.* 400 s indicating that some continuous oxidation currents can be realized at Pt with this compound despite an anodic current peak being exhibited in the voltammogram (Fig. 7), similar to that with phenol and 2-chlorophenol.

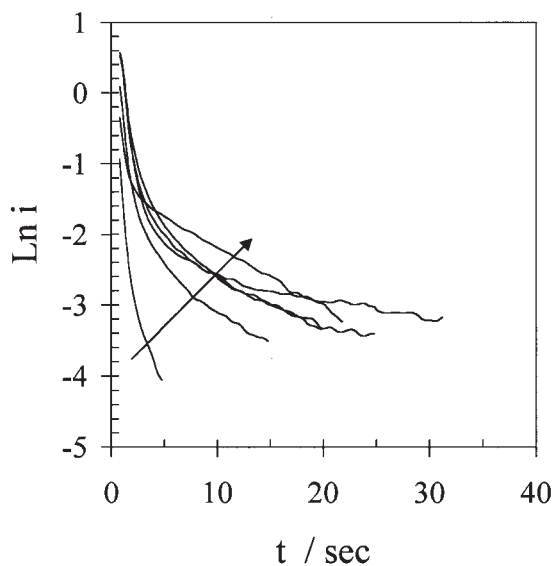


Fig. 11. Smoothed plots of $\ln i_v$ vs. t derived from the data plotted respectively in the curves of the inset of Fig. 10. (Direction of arrow corresponds to that in the inset of Fig. 10 for increasing response currents).

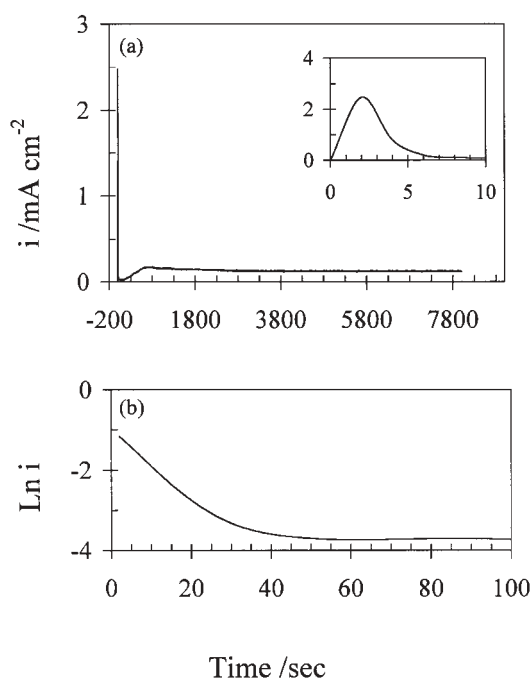


Fig. 12. a) Chronoamperometric current–time transients for oxidation of 0.01 M phenol in 1.0 M aq. NaOH at a Pt gauze electrode and b) $\ln i_v$ plotted vs. t .

2-Chlorophenol also exhibits a well-defined transient current maximum like that for phenol, but with no residual anodic current being sustained beyond *ca.* 50 s into the transient. Again, this is consistent with the clearly observed anodic current peak in this compound's voltammogram (Fig. 6).

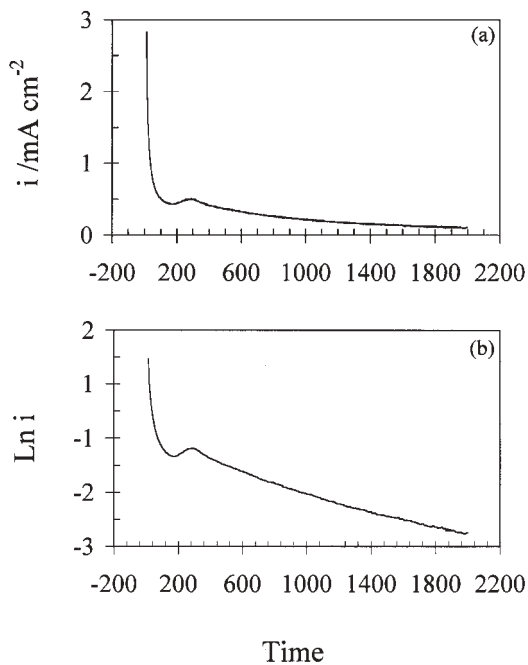


Fig. 13. Potential-step chronoamperometry for the electro-oxidation of 0.01 M catechol in 1.0 M aq. H_2SO_4 at a Pt gauze electrode.

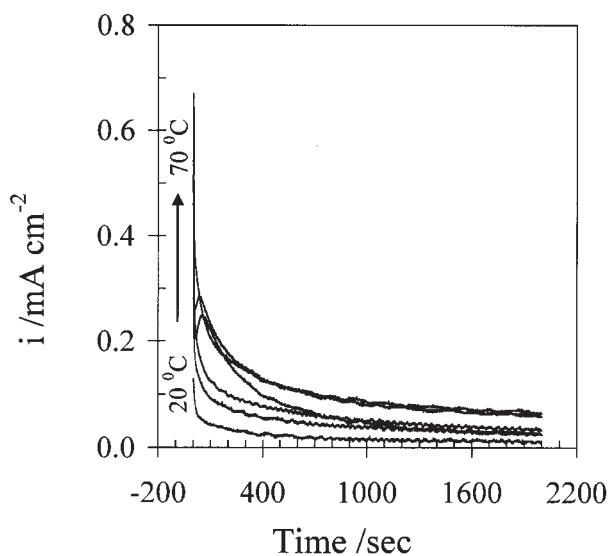


Fig. 14. Chronoamperometric current-time transients for oxidation of 0.1 M 4-chlorophenol in 0.1 M aq. H_2SO_4 at a Pt gauze electrode as a function of temperature, range 20 to 70 °C. Inset shows forms of plots up to 200 s into the transients.

For the purpose of comparative reference, chronoamperometric transients are shown in Fig. 15 for surface-oxide formation alone at the Pt electrode for temperatures between 20 °C and 70 °C (*cf.* Fig. 14 for 4-chlorophenol oxidation). The transients fall close upon one another since the temperature dependence of oxide-film formation at Pt

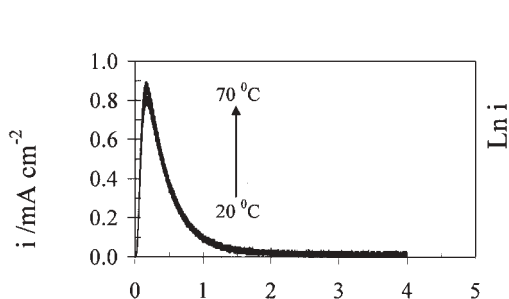


Fig. 15. Chronoamperometric current-time transients of 0.1 M aq. H_2SO_4 at a Pt gauze electrode in the absence of an organic as a function of temperature.

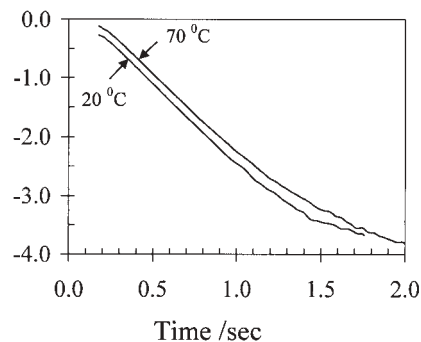


Fig. 16. $\ln i_v$ plotted vs. t from the data of Fig. 15 for the Pt gauze electrode in the absence of organic, (Note initial linear region up to $t \approx 1$ s).

is known to be small. Analysis by means of Eq. (3) gives the \ln plot of i_v vs. time shown in Fig. 16. Contrary to the case with the phenols, Eq. (1) applies here moderately well, with θ approaching a value for a true monolayer, initially of O species on the Pt anode, as known from other earlier works.^{18,20,21}

Earlier in this Section, we have referred to a possible analogy between the multilayer growth of a polymeric phenolic film and progressive nucleation and growth of cathodically deposited metals.^{25,26} Several equations developed in Refs. 25 and 26 apply to this situation. In Fig. 17 and 18, we show how test plots of current vs time func-

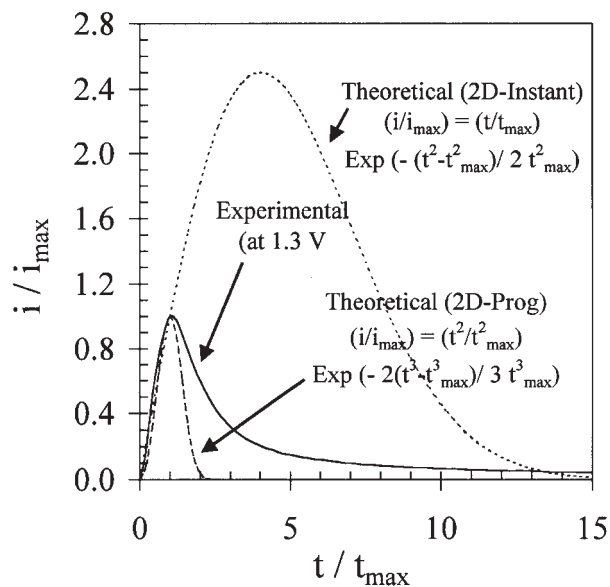


Fig. 17. Test plots for growth kinetics of the phenolic film at Pt according to 2-D nucleation and growth equations of Refs. 25 and 26.

$$(i/i_{\max})^2 = (1.9542/(t/t_{\max})) (1 - \text{Exp}(-1.2564 (t/t_{\max})))^2 \quad \text{3D-Instant}$$

$$(i/i_{\max})^2 = (1.2254/(t/t_{\max})) (1 - \text{Exp}(-2.3367 (t/t_{\max})^2))^2 \quad \text{3D-Prog}$$

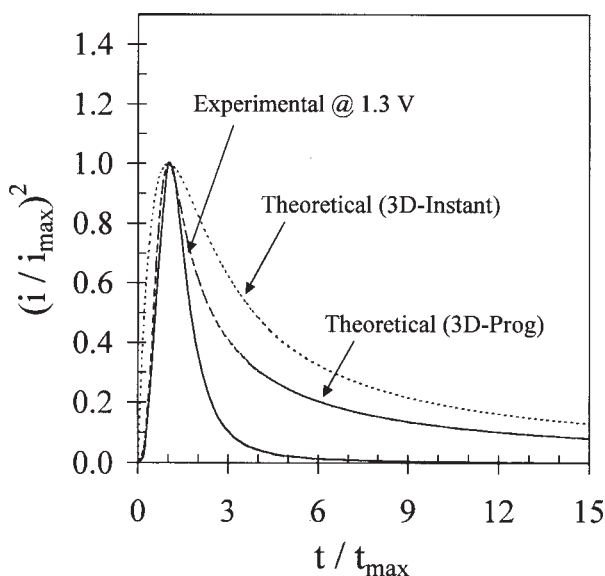


Fig. 18. Test plots for growth kinetics of the phenolic film at Pt according to 3-D nucleation and growth equations of Refs. 25 and 26.

tions for 2D and 3D instant and progressive nucleation compare with the experimental chronoamperometric transients. The 2D case (Fig. 17) does not provide any good fit to experiment as may be expected since multilayer growth is indicated. However, the test plots for the 3D case, shown in Fig. 18, give a much better representation of the experimental transient curves for surface blocking by the phenolic species in a multilayer.

The respective growth transient equations (Refs. 25, 26) are written on the respective diagrams. Note that for the autoinhibition by the phenolic film, passage of continuous finite currents at long times, such as can arise in metal deposition, is not to be expected (see experimental curves in Figs. 17 and 18) since complete blocking by the film already sets in after short times. Thus, in metal deposition, cathodic currents can continue to pass at the already nucleated and grown initial crystallites, that fully cover the substrate surface.

4. CONCLUSIONS

Electrochemical procedures can be applied to removal of noxious impurities, *e.g.*, heavy-metal ions or organics, by Faradaic reduction or electrocatalytic anodic oxidation procedures. These have the advantage that electrons (at cathodes) or electron-vacancy states (at anodes) are effectively the reagents for the electrochemical clean-up process,^{1,28} so that no additional reagent is required, except an inert supporting electrolyte.

Phenols and related compounds are regarded as serious pollutants of some industrial waste-waters and their removal has been the subject of direct-adsorptive proce-

dures on high-area charcoals or C felts and of direct electro-oxidative methods. With phenols, the latter procedures are subject to self-inhibition effects due to formation of polymeric films on the electrode surface. By means of cyclic voltammetry and chronoamperometric experiments, the electrochemical behaviour of such films can be quantitatively evaluated. The results obtained for several phenolic compounds enable comparisons to be made between their electrochemical surface reactivities and film-formation characteristics. The behaviour of hydroquinonoid adsorbates is quite different from that of phenol and chloro-substituted phenols, film formation tendencies being absent. This is due to the preferred reversible redox process of hydroquinone/quinone interchange that can arise with catechol and benzoquinone.

The polymeric films that are anodically generated from regular phenolic type compounds at Pt are very refractory towards strong electrochemical oxidizing conditions (elevated anode potentials and temperatures) so that continuous Faradaic oxidizing currents, that could lead to destruction of the phenolic compounds, cannot be maintained for any length of time, at least at Pt or oxidized Pt surfaces. Also, separately generated films of Pt surface oxide, formed up to 2.2 V (RHE), are unreactive towards phenols in solution.

Acknowledgment: Support of this work by the Natural Sciences and Engineering Research Council of Canada on a Strategic Grant is gratefully acknowledged.

ИЗВОД

ЕФЕКТИ САМО-ИНХИБИЦИЈЕ У РЕАКЦИЈИ АНОДНЕ ОКСИДАЦИЈЕ ФЕНОЛА ЗА ЕЛЕКТРОХЕМИЈСКО ПРЕЧИШЋАВАЊЕ ОТПАДНИХ ВОДА

H. AL-MAZNAI и B. E. CONWAY

Department of Chemistry, University of Ottawa, 10 Marie Curie Street, Ottawa, ON. K1N 6N5, Canada

Један од највећих изазова у науци о заштити животне средине је уклањање или модификација штетних органских нечистоћа. Посебна пажња се поклања загађивачима као што су: феноли, деривати фенола и полихлоровани бифеноли (PCB). У последње време изучавана је могућност директне електрокаталитичке оксидације оваквих нечистоћа на електродама са нанетом платином или рутенијум-диоксидом, које имају веома развијене површине. Међутим, у бројним случајевима, посебно код нечистоћа на бази фенола, њихову потпуну оксидацију спречава блокирање електродне површине полимеризованим продуктима оксидације и то доводи до само-инхибиције (пасивације) жељене електродне реакције. У раду су изучавани примери оваквих ефеката само-инхибиције, коришћењем метода линеарне промене потенцијала и хроноамперометрије.

(Примљено 27. августа 2001)

REFERENCES

1. E. Rudd, B. E. Conway, *Proc. Electrochemical Society Symposium on Water Purification by Photocatalytic, Photoelectrochemical and Electrochemical Procedures*, 94–19 (1994), T. L. Rose, O. Murphy, Eds., The Electrochemical Society, Pennington, N. J.
2. K. Rajeshwar, J. G. Ibanez, *Environmental Electrochemistry*, Academic Press, 1997 (ISBN No. 0-12-576260-7)

3. B. E. Conway, H. Al-Maznai, *Proc. 8th Fischer Symposium*, Karlsruhe, Germany, 2000, in press in *Electrochim. Acta* (2001)
4. H. Sharifian, D. W. Kirk, *J. Electrochem. Soc.* **133** (1980) 921
5. C. Comminellis, G. Pulgarin, *J. Appl. Electrochemistry* **22** (1992) 108
6. A. B. Boscoletto, F. Gottardi, A. de Battisti, G. Battaglin, *J. Appl. Electrochemistry* **24** (1994) 1052
7. R. N. Adams, in *Electrochemistry at Solid Electrodes*, Marcel Dekker, New York, 1969, pp. 363–365
8. B. E. Conway, B. V. Tilak, *Adv. In Catalysis* **38** (1992) 1, Academic Press, New York
9. A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980, (ISBN. No. 0-471-05542-5)
10. A. Merzbacher, E. F. Smith, *J. Am. Chem. Soc.* **22** (1900) 723
11. E. Ayranci, B. E. Conway, *Anal. Chem.*, in press (2001)
12. R. W. Coughlin, F. S. Ezra, *Environmental Science and Technology* **2** (1969) 291
13. V. L. Snoeyink, in *Chemistry of Water Supply, Treatment and Distribution*, Ann Arbor Sci., Ann Arbor, MI., 1974
14. P. Magne, P. L. Walker, *Carbon* **24** (1986) 101
15. R. Prober, J. J. Pycha, W. E. Kidon, *AIChE J.* **21** (1975) 1200
16. R. D. Vidic, *Water Research* **24** (1990) 1187
17. R. D. Vidic, M. D. Suidan, G. A. Sorial, R. C. Brennev, *Water Environmental Research* **65** (1993) 156
18. B. E. Conway, R. Barnett, H. A. Kozłowska, B. V. Tilak, *J. Chem. Phys.* **93** (1990) 8361
19. B. Pierozynski, S. Morin, B. E. Conway, *J. Electroanal. Chem.* **467** (1999) 30
20. H. A. Kozłowska in *Comprehensive Treatise on Electrochemistry*, Vol. 9, Chapter 2, J. O'M. Bockris, E. Yeager, B. E. Conway, Eds. Plenum Publ. Co., New York, 1981
21. B. E. Conway, H. A. Kozłowska, W. B. A. Sharp, *J. Electroanal. Chem.* **43** (1973) 9
22. B. E. Conway, *Progress in Surface Science* **49** (1995) 331
23. A. Streitwieser, C. H. Heathcock, *Introduction to Organic Chemistry*, Macmillan Publ. Co., New York, 1976, p. 1026
24. B. E. Conway, *Ionic Hydration in Chemistry and Biophysics*, Elsevier Publ. Co., Amsterdam 1981
25. M. Fleischmann, H. R. Thirsk, in *Adv. in Electrochem. and Electrochem. Eng.*, Vol. 3, P. Delahay, C. W. Tobias, Eds., Interscience, New York, 1963, p. 123
26. M. Fleischmann, H. R. Thirsk, *Electrochim. Acta* **2** (1960) 22
27. M. Avrami, *J. Chem. Phys.* **8** (1940) 212
28. *Proc. Electrochemical Society Symposium on Electrochemical Contributions to Environmental Protection* (various papers), T. R. Beck, C. G. Enke, O. B. Cecil, J. McCallum, S. T. W. Lodek, Eds., The Electrochemical Society, Pennington, N. J., 1972.