

Indirect Electrochemical Oxidation of Phenol by Ce^{4+} , Controlling Surface Insulation of Au Electrode

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Indirect electrochemical oxidation of phenol by Ce^{4+} was investigated in sulfuric acid solutions. It was found that electrode fouling during oxidation of phenol can be controlled by adjusting the time interval (TI) of double potential steps (DPSs). While the electroactivity was greatly decreased after several DPSs of a relatively long TI, repeated DPSs with a short potential pulse showed substantial amounts of electroactivity after a few hundreds or thousands DPS, suggesting that the formation of an insulating layer can be controlled by adjusting a potential program. Effectiveness of the consecutive application of DPSs for phenol decomposition was confirmed by GC-MS.

Key Words : Electrochemical oxidation, Phenol, Electroactivity, Surface

Introduction

Removal of phenolic hydrocarbons from wastewater prior to their discharge is a prerequisite in many chemical-manufacturing industries since they can be fatal to the environment or human health even at ppb levels.¹ A number of studies have been carried out to decompose phenolic pollutants dissolved in wastewater during the last few decades.² Ultrasonic irradiation³ in conjunction with other methods such as addition of TiO_2 ,⁴ photochemistry,⁵ and ozonation⁶ was utilized for the decomposition of phenolic compounds, in which the cavitation process generates reactive free radicals responsible for chemical oxidation of organic pollutants. Biological treatments of wastewater such as microbial⁷ and enzymatic⁸ oxidations are probably the most environmentally compatible method, but it often requires pretreatment for high concentrations of organic pollutants and may result in the generation of hazardous by-products.

Direct or indirect electro-oxidation of organic compounds was also studied. While the electron transfer takes place between electrodes and decomposable species in direct electrochemical oxidation, indirect oxidation mainly uses electrochemically oxidized species as mediators for the destruction of organic compounds. For indirect electro-oxidation, destruction of organic compounds by anodically generated chlorine and hypochlorite is well known.⁹ Reactive and high-valent metal ions which are electrochemically generated from stable and low valent state were also utilized to degrade organic pollutants. Various redox couples such as Ag^+/Ag^{2+} ,¹⁰ Co^{2+}/Co^{3+} ,¹¹ Fe^{2+}/Fe^{3+} ,¹² and Ce^{3+}/Ce^{4+} ^{13,14} were examined as mediators.

In this paper, we describe electrochemical oxidation of phenol mediated by Ce^{3+}/Ce^{4+} redox couples. It is well known that passivation occurs during electrochemical decomposition of phenol, depositing an insulating film on the electrode surface.¹⁵ Although side products such as

catechol and hydroquinone are produced, the formation of insulating layers has been a main obstacle for electrochemical decomposition of phenol.¹⁶ Wang *et al.* quantitatively studied the formation of a polyphenol film on Au, utilizing an electrochemical quartz crystal microbalance. The complete coverage of the electrode by an insulating film was addressed regardless of the phenol concentration and the potential-sweep rate.¹⁷ In this work, we examined passivation behaviors as a function of phenol and Ce^{3+} concentrations and, to our best knowledge, first address the control of an insulating layer formation by simply adjusting potential-application methods.

Experimental Section

Sulfuric acid, phenol, Cerium(III) chloride, $CHCl_3$, and H_2SO_4 purchased from Aldrich Chemical Co., were used as received. Water was purified through a Milli-Q Plus system (Millipore Co.) until its resistivity was over 18 M Ω cm.

For the measurement of electroactivity changes due to surface passivation, Au button electrode (geometrical area = 0.02 cm²) was used as the working electrode. The reference electrode was Ag/AgCl (3M KCl) and the counter electrode was a platinum flag. All electrochemical measurements were performed with a CV-50W electrochemical analyzer (Bioanalytical Systems).

In order to confirm the decomposition of phenol by GC-MS, a Au plate of a relatively large area (geometrical area = 2.8 cm²) was placed in a 0.1 M H_2SO_4 solution (1.0 mL) containing 2 mM phenol and 5 mM Ce^{3+} . After electrochemical treatments, organic components were extracted with excess amounts of $CHCl_3$. The volume of $CHCl_3$ solutions was then reduced to 0.1 mL by evaporation at ambient conditions and a 5 μ L $CHCl_3$ solution of 0.090 M toluene was added as an internal standard. An HP 5890 gas chromatograph with split injection (200 °C; 1 : 17), coupled to a HP 5972 mass selective detector, was utilized for the

separation on an Agilent HP-5MS capillary column (30 m \times 0.25 mm \times 1 μ m). The oven temperature was raised at 10 $^{\circ}$ C/min to 180 $^{\circ}$ C after 2 min isotherm at 50 $^{\circ}$ C.

Results and Discussion

In order to investigate the effect of phenol concentrations on electrode passivation, cyclic voltammetry was carried out in 0.1 M H₂SO₄ aq. solutions containing 5 mM Ce³⁺ and various concentrations of phenol. Figure 1 shows voltammograms of 1st and 5th cycles in (A) 5 mM, (B) 2 mM, and (C) 0.5 mM phenol solutions at 50 mV/s. When the phenol concentration is relatively high (Figure 1A), complete deactivation of the electrode surface occurs during the first positive scan. No Ce³⁺ oxidation peak is seen at a potential range higher than 1.0 V and the current response due to direct phenol oxidation is also rapidly decreased indicative of an insulating layer formation. Subsequent cycles show only negligible current responses.

The complete insulation of the surface is alleviated as the decrease of phenol concentrations. During the first positive

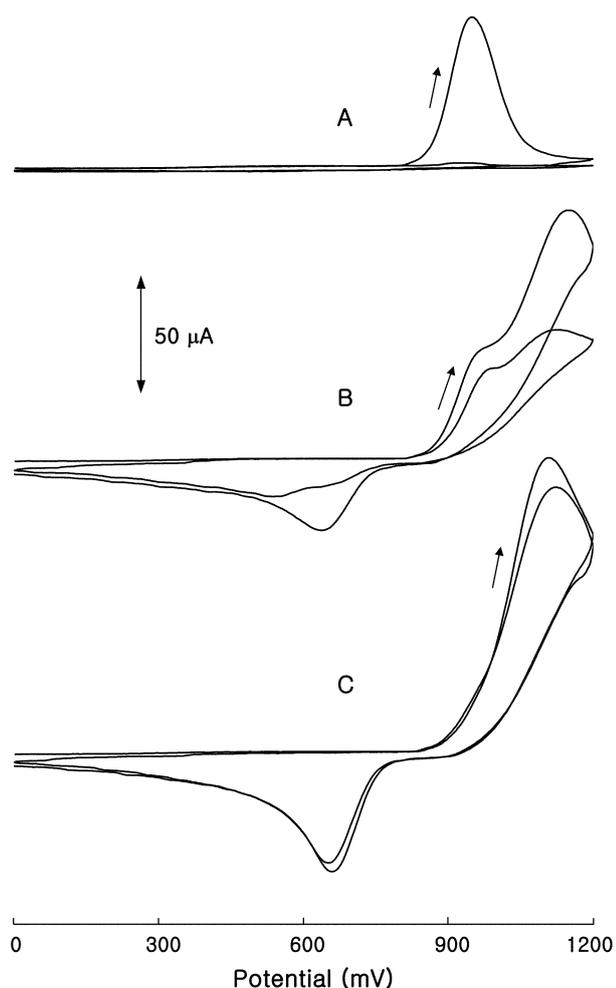


Figure 1. Cyclic voltammograms of 0.1 M H₂SO₄ solutions containing 5 mM CeCl₃ and various concentrations of phenol at 50 mV/s. 1st & 5th scans are shown. (A) 5 mM, (B) 2 mM, and (C) 0.5 mM phenol.

scan in a 2 mM phenol solution, a distinct Ce³⁺ oxidation process after direct oxidation of phenol occurs, indicating that the surface insulation is incomplete (Figure 1B). Corresponding cathodic peak of a Ce^{3+/4+} couple is also shown at ca. 650 mV during the first reverse scan. Continuous potential cycling, however, results in a gradual decrease of electroactivity as shown in Figure 1B. Further decrease of phenol concentrations leads to no substantial decrease of electroactivity during the first few cycles. Figure 1C shows the voltammogram of 0.5 M phenol and 5 mM Ce³⁺, which is quite similar to that of a phenol-free solution.

It should be mentioned that the rate of passivation processes also depends on Ce³⁺ concentrations. Cyclic voltammogram performed in a solution of 2 mM phenol but with no Ce³⁺ exhibits similar behaviors to Figure 1A and the increase of Ce³⁺ concentrations retards the surface insulation. Compared with direct oxidation of phenol, this behavior seems to indicate that, as the increase of Ce³⁺, phenol oxidation at the solution phase becomes more important rather than that near the solution/electrode interface. This can be realized when the electron transfer rate between Ce^{3+/4+} is faster than the decomposition rate of phenol by Ce⁴⁺.

Although surface passivation can be alleviated by adjusting phenol and Ce³⁺ concentrations, repeated potential cycling (or continuous oxidation at a fixed potential) leads to surface insulation in effect. In addition, the control of [phenol]/[Ce³⁺] may be meaningless from a practical point of view since the concentration range of phenol which must be treated before discharge is from 2000 ppm to a few ppb¹⁸ and excess use of Ce³⁺ may give rise to other environmental problems. Therefore, we chose 5 mM Ce³⁺ and 2 mM phenol (188 ppm) in this study to elucidate the effects of applying potentials to the electro-oxidation of phenol.

Figure 2 exhibits anodic charge responses during double potential steps (DPSs) in between 0 V and 1.2 V with different time intervals (TIs). After applying 1.2 V for a fixed TI, the potential was returned to and maintained at 0 V until the next DPS. The time at 0 V was a slightly longer than the specified TI due to data processing. When the time subject to the oxidation of phenol at 1.2 V is 20 sec (Figure 2A), the appreciable amount of anodic charges during 1st DPS is greatly reduced at 2nd DPS. This trend continues during subsequent DPSs, although the magnitude of electroactivity decrease becomes smaller (Figure 2A 3rd, 4th, and 5th). Figure 2B demonstrates anodic charge responses during 1st, 21st, 41st, 61st, and 81st DPS performed with TI of 1 sec. These chronocoulometric results were chosen to directly compare electroactivity changes with those in Figure 2A. For example, charge responses during 21st DPS in Figure 2B were obtained on the electrode that was previously treated at 1.2 V for 20 sec in total (*i.e.*, 20 DPSs \times 1 sec). This makes it meaningful to compare the charge difference between 1st and 2nd DPS in Figure 2A with that between 1st and 21st DPS in Figure 2B. From Figure 2, it is obvious that the surface insulation can be controlled by adjusting TI of DPS. While charge responses are reduced to

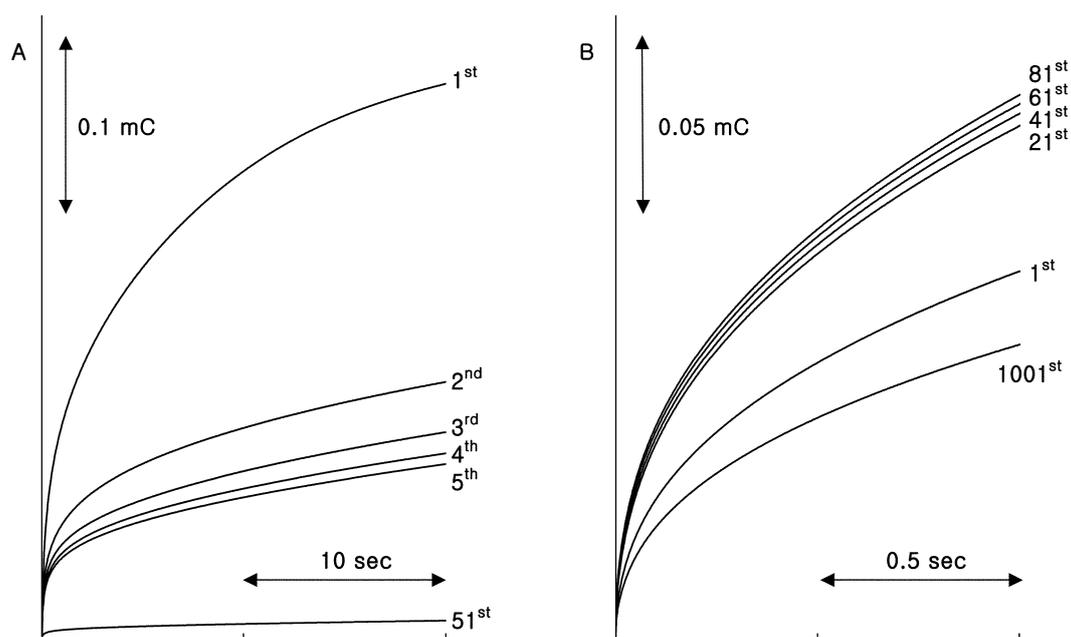


Figure 2. Anodic charge responses during DPS in 0.1 M H_2SO_4 solutions containing 5 mM $CeCl_3$ and 2 mM phenol. (left) TI = 20 sec. (right) TI = 1 sec.

ca. 30% at 5th DPS with TI of 20 sec, electroactivity is rather increased by *ca.* 47% at 81st DPS with 1 sec TI. This initial increase of electroactivity reaches a maximal value followed by slow decrease. It is worth mentioning that electrodes retain *ca.* 70-80% of initial electroactivity after 1000 DPS in

the case of Figure 2B, but virtually no faradaic charge appears to pass for 51st DPS in Figure 2A.

In order to compare the extents of surface insulation at various TIs, we utilized 10 mM $K_4[Fe(CN)_6]$ dissolved in 0.1 M NaCl solutions as an electrochemical probe. Cyclic voltammetry was carried out on electrodes treated in 0.1 M H_2SO_4 solutions of 2 mM phenol and 5 mM Ce^{3+} at 1.2 V for 100 sec in total. Figure 3 shows cyclic voltammograms obtained on electrodes subject to (A) 100 DPS (1 sec TI), (B) 50 DPS (2 sec TI), (C) 20 DPS (5 sec TI), (D) 5 DPS (20 sec TI), and (E) no DPS (100 sec at 1.2 V). Figure 3 indicates that the peak currents decrease as the increase of TIs, leading to complete blocking of electron transfer for the electrode no potential pulse was used (Figure 3E).

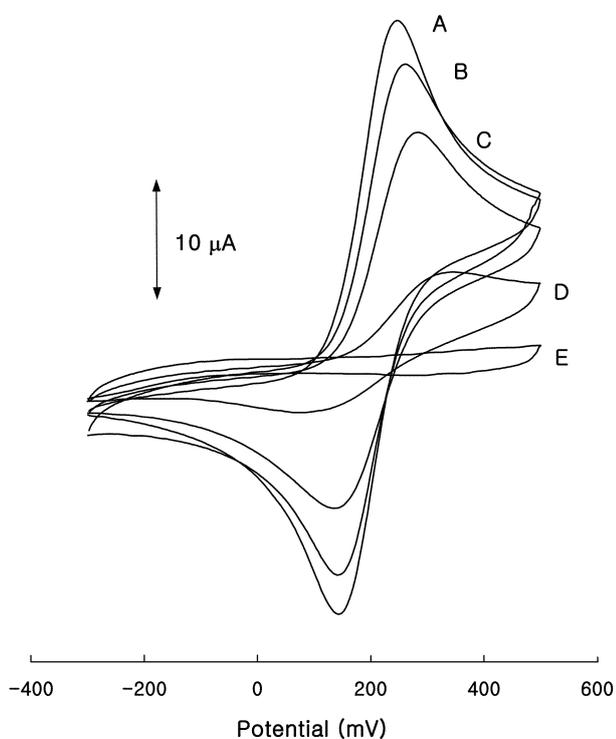


Figure 3. Cyclic voltammograms of 10 mM $K_4[Fe(CN)_6]$ in 0.1 M NaCl on electrochemically treated electrodes in 0.1 M H_2SO_4 solutions containing 5 mM $CeCl_3$ and 2 mM phenol. (A) 100 DPS, 1 sec TI, (B) 50 DPS, 2 sec TI, (C) 20 DPS, 5 sec TI, (D) 5 DPS, 20 sec TI, and (E) no DPS, 100 sec at 1.2 V.

We observed the formation of dark-yellowish films for DPS of short TIs, which is different from transparent films produced when the oxidation potential of relatively long TIs (1.2 V in this study) is applied. The reason for the difference with TIs is not clear at this point, but it appears to imply the followings: First, polyphenol formation by direct oxidation seems to be limited by quickly reversing the potential. It has been known that polyphenol is produced through a step-polymerization mechanism,¹⁹ in which high molecular weight polymers are formed at the end of the reaction. Note that mediated oxidation also accompany the direct electron transfer between electrodes and phenol molecules. Second, indirect electrochemical oxidation of phenol by Ce^{4+} appears to produce different chemical species rather than polyphenol by direct oxidation. It is likely since surface insulation is alleviated with the increase of Ce^{3+} concentrations as described above.

Since, although electroactivity is maintained with DPS of short TIs, it does not necessarily mean the effectiveness of phenol decomposition, we examined phenol concentration

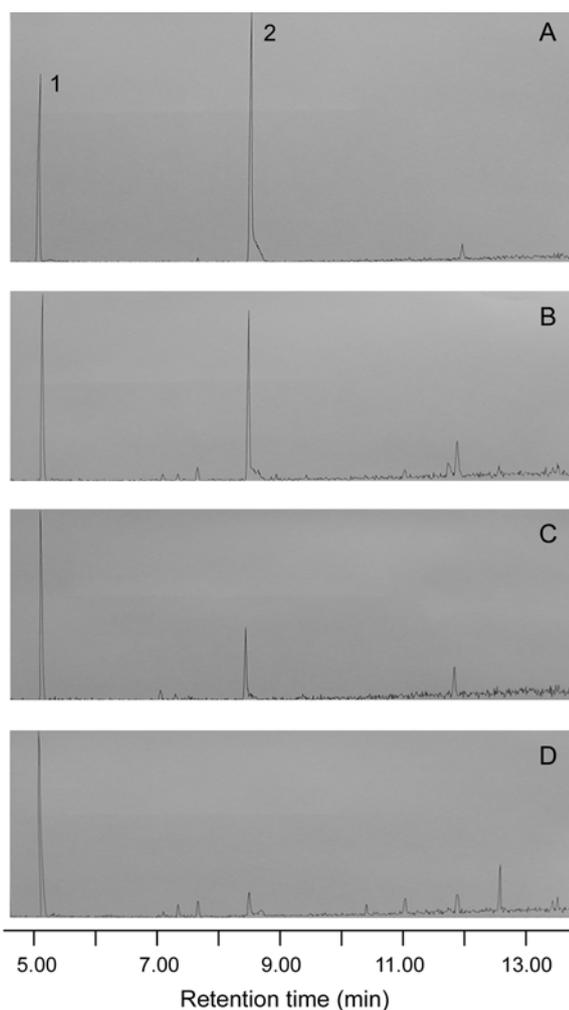


Figure 4. Gas chromatograms of concentrated phenol solutions after electrochemical treatments. Indirect oxidation was performed in 0.1 M H_2SO_4 solutions containing 5 mM CeCl_3 and 2 mM phenol by applying (A) no DPS (1000 sec at 1.2 V), (B) 50 DPS (20 sec TI), (C) 200 DPS (5 sec TI), and (D) 1000 DPS (1 sec TI). Internal standard (toluene, peak 1) was added into concentrated CHCl_3 solutions as described in the experimental section. Phenol and toluene were identified from MS data and no further analysis was performed for side products. The reduction of peak 2 heights as the decrease of TIs suggests that phenol decomposition without insulating layer formation on the electrode surface can be accom-

plished by a DPS method suggested here. The areas of peak 2 relative to peak 1 are (A) 1.72, (B) 0.86, (C) 0.32, and (D) 0.09, indicating that the phenol concentrations were reduced from 2 mM to (A) 2.0, (B) 1.0, (C) 0.37, and (D) 0.10 mM after electrochemical treatments. The chromatogram of an untreated solution showed only negligible difference from Figure 4A.

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Conclusions

Indirect electrochemical decomposition of phenol is usually hampered by an insulating layer formation on the electrode. Although electrode passivation can be partially controlled by increasing mediator concentrations, it may cause other environmental problems. This can be circumvented by applying consecutive short potential pulses rather than constant or sweeping potentials. Utilizing DPSs of short TIs, it was confirmed that more than 95% of phenol could be decomposed without substantial loss of electroactivity.

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