Investigation on the Electrochemical Polymerization of Catechol by Means of Rotating Ring-disk Electrode

KONG, Yong(孔泳) MU, Shao-Lin*(穆绍林)
Department of Chemistry, Yangzhou University, Yangzhou, Jiangsu 225002, China

The electrolysis of catechol was studied in the pH values of 1 to 10. The results from the rotating ring-disk electrode (RRDE) experiments show that at low pH values, the electrochemical polymerization of catechol was performed by one step, and at higher pH values, the electrochemical polymerization of catechol was carried out by two steps, *i.e.* oxidation of catechol and followed by polymerization. The intermediates generated at the disk were detected at the ring electrode in the ring potential region of −0.2 to 0 V (vs. Ag/AgCl). One of reasons for the decrease in the ratio of i_r to i_d with increasing the ring potential is caused by formation of positively charged intermediates at the disk electrode. This ratio increases with increasing the rotation rate of the RRDE, which indicates that the intermediates are not stable. A shielding effect during polymerization of catechol was observed when the ring potential was set at 0.1 V (vs. Ag/AgCl). The electron spin resonance (ESR) of polycatechol shows that polycatechol possesses unpaired electrons. The images of polycatechol films synthesized at different conditions are described.

Keywords electrochemical polymerization, catechol, rotating ring-disk electrode, intermediates, electron spin resonance, scanning electron micrographs

Introduction

The electrochemical polymerization of phenol and its derivatives in the weak basic solutions and alcohol media has been studied extensively by Pham and Lacaze *et al*.[1-3] using various metals as working electrodes. This is due to the fact that a passivating layer was formed on the metal surface during the electrolysis process, which plays an important role in protecting metals from corrosion.[4,5] These passivating layers are insulators without the electrochemical activity. This was caused by the over-oxidation of the polymer because the polymerization of the monomer was carried out in a large scan potential range of −0.2 to 2.0 V (vs. SCE).[5]

However, polymers from the electrochemical polymerization of catechol derivatives on carbon substrates are electroactive, and have been used as biosensor material and a mediator for the redox couple of NAD^+/NADA.[6-8] Davis *et al*.[9] reported the electrochemical polymerization of catechol and its derivatives on a glassy carbon electrode and the effect of ethylene diamine on the polymerization of catechol and the property of polymers. Recently, Cortes *et al*.[10] reported the polymerization of catechol on the silver surface using surface-enhanced Raman spectroscopy, in which a possible polymerization mechanism was suggested.

Phenol in NaOH solution (3 mol/L) can be polymerized on platinum at the scan potential range of 0 to 0.8 V (vs. SCE). And its film grows quickly with time during the electrolysis process.[11] Polyphenol obtained in this condition has a conductivity of 1.2×10^{-4} S/cm, but has no electrochemical activity. We found that polycatechol on platinum obtained from repeated potential cycling between 0 and 1.2 V (vs. SCE) is still electroactive. Above results indicate that whether polycatechol has electroactivity or not is strongly dependent on the electrode material, applied potential and the composition of the solution used. So the electrochemical polymerization of catechol is rather complicated.

To gain a better understanding of the polymerization mechanism of catechol, we try to use rotating ring-disk electrode (RRDE) to study the electrochemical polymerization of catechol. This is due to the fact that RRDE experiment can provide a richness of information about the formation, detection and decay of an intermediate.[12] Also this technique can easily identify whether an intermediate generated at the disk electrode is charged or not by varying the ring electrode potential.[13] In this paper, the effects of the ring potential, rotation rate, potential scan rate and pH value of the electrolytic solution on the electrolysis behavior of catechol, ESR spectrum and image of polycatechol have been reported.

Experimental

The chemicals used were all of reagent grade. Doubly distilled water was used to prepare solutions. The pH values of the solutions were measured using a Model PXD-12 pH meter. A Model HR-103A (Japan) rotating ring-disk electrode (RRDE) was used for the investigation on the

* E-mail: slmu@yzu.edu.cn
Received December 12, 2001; revised November 26, 2002; accepted February 17, 2003.
Project supported by the National Natural Science Foundation of China (No. 20074027).

electrochemical polymerization of catechol. The electrolysis cell consisted of a platinum disk electrode, a platinum ring electrode, a platinum counter electrode and a reference electrode of Ag/AgCl with saturated KCl solution.

The diameter of the platinum disk electrode is 7.89 mm. The collection efficiency of the RRDE is 0.419. A Model HPD-1A bipotentiostat was used for the electrolysis of catechol. The disk current and ring current as function of potential and time, respectively, were recorded simultaneously using a Model 3066 bipen recorder. The rotation rate of the RRDE was controlled between 500 and 3000 r/min. The sweeping potential range was set between 0 and 1.2 V. The UV-visible spectra of catechol and quinone, dissolved in the solution of NaCl (0.5 mol/L) and NaH_2PO_4 or Na_2HPO_4, (0.1 mol/L) were carried out using a Model UV-2501 PC (Shimadzu) spectrometer. The ESR spectrum of polycatechol was detected using an ESR spectrometer (JES-FEKG, Jeol). The images of polycatechol films polymerized on platinum were recorded using a Model Hitachi S-530 scanning electron microscope.

Results and discussion

Effect of the ring potential

To know whether an intermediate generated at the disk is charged or not, the ring potential was changed at 0.1 V interval from −0.2 to 0.2 V. The electrolysis of catechol was carried out using a RRDE. The electrolytic solution consisted of catecholc (0.2 mol/L), NaCl (0.5 mol/L) and Na_2HPO_4(0.1 mol/L) with pH = 8.72. The rotation rate was controlled at 1000 r/min. The potential scan rate was set at 50 mV/s. Here, three plots with different ring potentials to explain the effect of ring potential on the ring current are presented.

The plots A, B and C in Fig. 1 show the i_d-E and i_r-t curves obtained at the ring potentials of −0.2, 0.0 and 0.1 V, respectively. Curves 1, 2 and 3 in plots are the first, second and third scans, respectively. There are two peaks at 0.40 and 0.94 V on the i_d-E curve of each plot for the first scan. The first oxidation peak at 0.40 V is attributed to the oxidation of catechol. The second oxidation peak at 0.94 V is caused by the polymerization of catechol. Two corresponding reduction peaks occur on the i_r-t curve. This means that two soluble intermediates were generated at the disk electrode during the electrolysis of catechol. The feature that i_d-E curve and i_r-t curve at each plot have in common is that their peak currents decrease with increasing number of potential scans, and the potentials of two peaks shift towards more negative potentials from the first scan to the second scan. This is due to the fact that catechol was polymerized on the bare platinum for the first scan, however, catechol was polymerized on the polycatechol film itself for the second scan. That is, the oxidation potential and the polymerization potential of catechol were affected by the electrode material.

Plots A and B in Fig. 1 show that two soluble intermediates generated at the disk electrode were reduced at the ring electrode. Since their current values are negative, this is just contrary to the direction of the disk current.

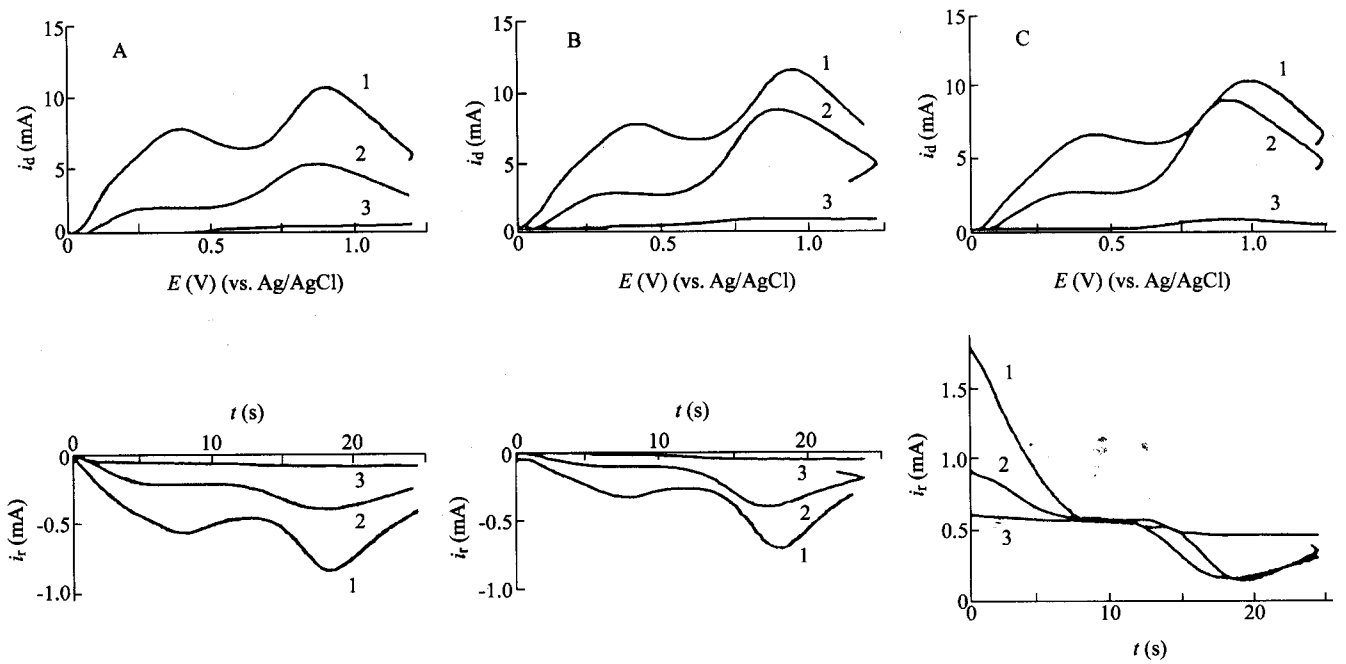
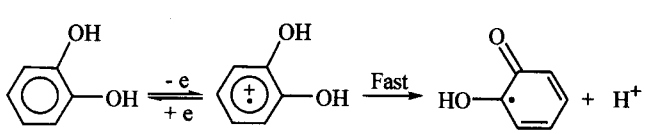


Fig. 1 Effect of the ring potential on the ring current. Ring potentials: (A) −0.20 V, (B) 0.0 V, (C) 0.10 V (vs. Ag/AgCl with saturated KCl solution). Curves: (1) first scan, (2) second scan, (3) third scan. The solution containing catechol (0.2 mol/L), NaCl (0.5 mol/L) and Na_2HPO_4 (0.1 mol/L) with pH = 8.72, 1000 r/min. Potential scan rate: 50 mV/s.

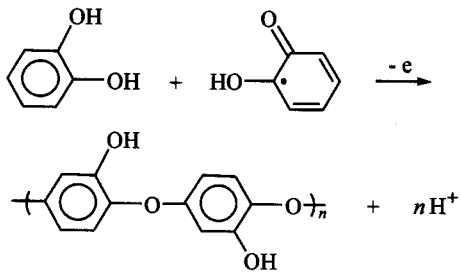
However, plot C in Fig. 1 shows that the ring current becomes positive at the beginning electrolysis, then decreases quickly as the disk potential continues to scan and finally a peak is formed on the i_r-t curve. The former is caused by the oxidation of catechol, because the ring potential is set at 0.1 V in this case. The result is in good agreement with that at the disk electrode, since the oxidation current of catechol on the disk was observed at 0.1 V. The latter is caused by shielding effect, since as the disk potential continues to scan towards the positive direction, the oxidation rate of catechol at the disk increases with increasing potential, so the flux of catechol to the ring decreases. This effect results in decrease of the ring current. When the anodic peak at 1 V occurs on the i_d-E curve, the flux of catechol to the ring is minimal. Thus, a corresponding anodic peak with the smallest current forms on the i_r-t curve.

Based on the data shown in Fig. 1, the ratio of the peak current of the ring electrode (i_r) to that of the disk electrode (i_d) at 0.4 and 0.9 V for the first scan was calculated, respectively, when the ring potential was set between −0.2 and 0 V. Both of the ratios are decrease with increasing the ring potential. This is mainly caused by the decrease in the ring current, while the disk current hardly changes. The latter is to be expected due to the disk current being independent of the ring potential. In this experiment, the contribution of migration of the electroactive species to mass transfer is small, because of an excess of the supporting electrolyte, but it can not be neglected completely at least in this case. This is due to the fact that the space between disk and ring is vary small, and the ratio of i_r/i_d is larger even the disk current is mainly attributable to formation of the polymer. For example, i_r/i_d is 0.14 at 0.4 V and 0.22 at 0.9 V when the ring potential is set at −0.2 V. The large ratio of i_r/i_d means that a appreciable amount of intermediates was collected at the ring electrode. In this case, the migration of the intermediates from the disk to the ring electrodes is still in existence more or less due to the potential difference between the disk and the ring electrodes. So, one of reasons for the decrease in the ratio of i_r/i_d with increasing the ring potential is caused by formation of positively charged intermediates at the disk electrode.

The electrochemical oxidation of hydroquinone is assumed to be a free radical reaction,[14] in which a reaction scheme for formation of the free radical with positive charge was presented. Thus, it is reasonable to assume that the electrochemical oxidation of catechol at the beginning stage could produce a radical with positive charge:



The polymerization mechanism of catechol is assumed as follows:



The structure of the polymer is suggested elsewhere.[15]

Effect of pH *on electrolysis of catechol*

The electrolytic solution consisted of catechol (0.2 mol/L), NaCl (0.5 mol/L) and Na_2HPO_4(0.1 mol/L) or NaH_2PO_4. The pH value of this solution was set at 1.03, 5.78, 6.88, 8.72 and 10.12. Here three plots with different pH values to express the effect of pH on the electrochemical polymerization of catechol are presented.

The potential scan rate was set at 50 mV/s. The rotation rate of the RRDE was controlled at 1000 r/min. The ring potential was controlled at −0.1 V. Plots A, B, C and D in Fig. 2 show the results of the RRDE experiment at pH = 1.03, 5.78, 8.72 and 10.12, respectively. The i_d-E curve at each plot in Fig. 2 is different in shape as well as i_r-t curve. The disk current for the electrolysis of catechol at pH = 1.03 begins to rise at 0.6 V, and then increases quickly as the potential continues to scan towards the positive direction. An oxidation peak does not occur at 1.10 V till twentieth scan (Curve 5). The subsequent oxidation peak shifts towards the negative direction for the fortieth scan (Curve 6). This is caused by polymerization of catechol on polycatechol film itself, which has been mentioned earlier. The disk current decreases with increasing the number of potential scans. Also, the changes in a corresponding ring peak potential and ring current with the number of potential scans are observed. After electrolysis, a polycatechol film was found on the disk electrode.

Plot B in Fig. 2 shows results from the electrolysis of catechol at pH = 5.78. The disk current rises first at about 0.4 V, and then increases quickly beginning at 0.65 V for the first scan. Also, a corresponding ring current is observed. Plot C in Fig. 2 shows results from the electrolysis of catechol at pH = 8.72. Two oxidation peaks at 0.40 and 0.94 V occur on the i_d-E curve of the first scan (Curve 1). Also two corresponding reduction peaks occur on the i_r-t curve. This is different from Plots A and B, and also different from the electrolysis of catechol at pH = 6.88 (i_d-E and i_t-t curves omitted here). No oxidation peak at 0.4 V was observed on the i_d-E curve for the electrolysis of catechol at pH = 6.88, even its disk current rises beginning at 0.25 V. Plot D in Fig. 2 shows the results from electrolysis of catechol at pH = 10.12. An oxidation peak at 0.33 V occurs on the i_d-E curve for the first scan (Curve 1). The disk current decreases quickly as the potential is beyond this peak potential. This is much different

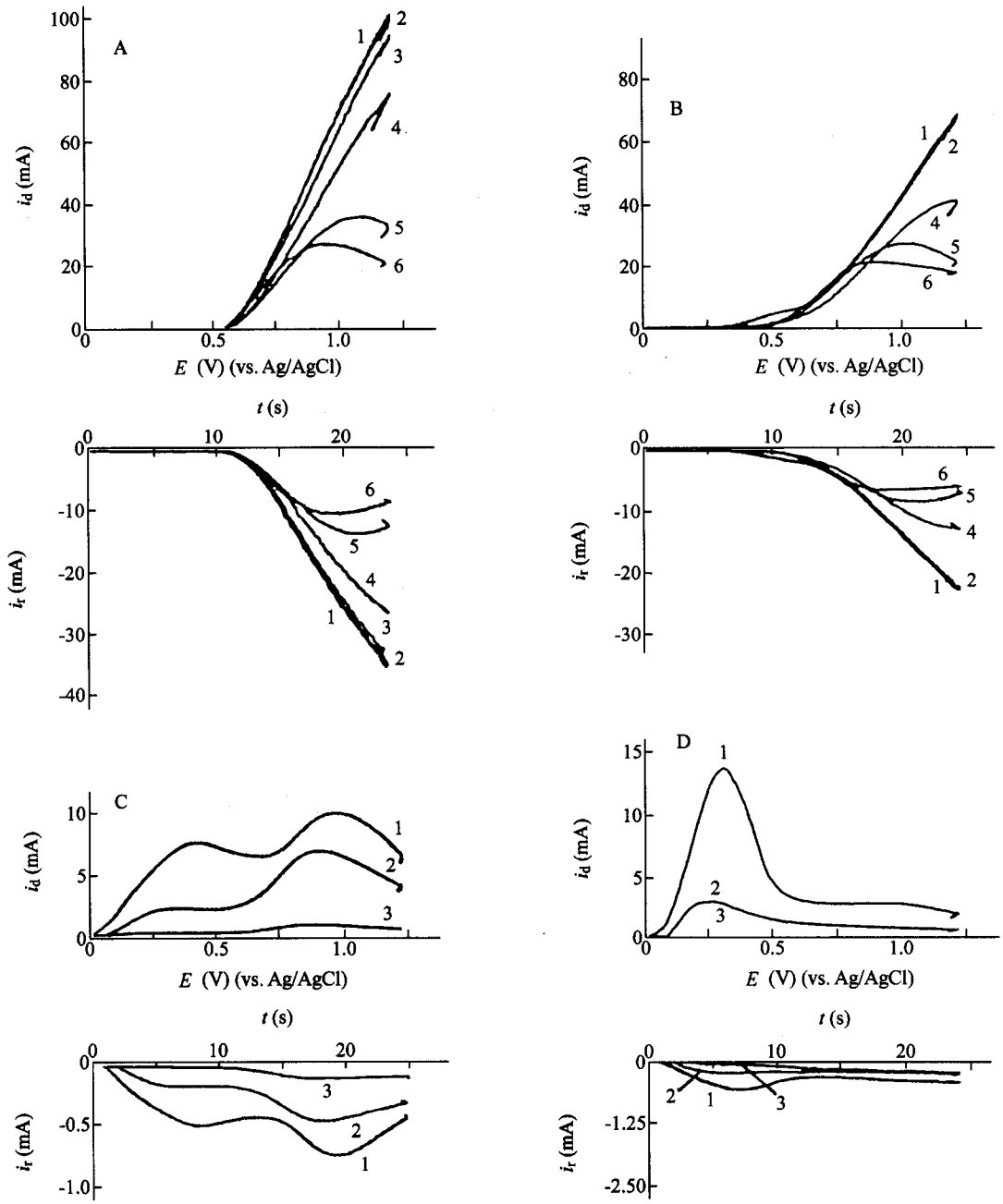


Fig. 2 Effect of pH on electrolysis of catechol. The electrolytic solution is the same as that shown in Fig. 1. Plots: (A) pH = 1.01, (B) pH = 5.78, (C) pH = 8.72, (D) pH = 10.12. Ring potential is set at − 0.1 V. Curves: (1) first scan, (2) second scan, (3) third scan, (4) tenth scan, (5) twentieth scan, (6) fortieth scan. 1000 r/min. Potential scan rate: 50 mV/s.

from those shown in Plots A, B and C. A corresponding reduction peak is also observed at the ring electrode. After electrolysis, no polymer film was found at the disk electrode. This means catechol can not be polymerized at pH = 10.12. Also, little intermediate is detected at potentials higher than 0.6 V.

The above results show that catechol is oxidized more easily at the basic solution than at the acidic solution and the basic solution is favorable for the formation of intermediates. The intermediate plays an important role in accelerating the oxidation and polymerization of catechol. The former is coincident with change in the solution color of catechol. A basic solution of catechol turns from colorless into yellow more quickly than an acidic solution of one in air, which is often observed in laboratory. To prove this suggestion, UV-visible spectra of a series of freshly prepared solutions of catechol, a catechol solution stored for 4 h and a fresh solution of quinone were recorded in Fig. 3. In this experiment, no electrodes were put in the solutions. In another words, the change in spectra is only caused by the chemical oxidation of catechol with oxygen in air. Spectrum lines 1, 2, 5 and 4 in Fig. 3 are spectra of freshly prepared solutions of catechol at pH = 1.03, 6.88, 8.72 and 10.12, respectively. The solution composition of catechol used in this experiment is the same as that mentioned above. It is clear that the absorbance in the

wavelength between 350 and 550 nm increases with increasing pH value, except pH = 10.12 (Curve 4). This indicates that the oxidation of catechol in the basic solution is easier than that in the acidic solution. A peak at 449 nm occurs on Curve 4. This is different from other spectrum lines. But this spectrum line is similar in shape to spectrum line 3 of quinone, in which a absorption peak occurs at 427 nm. Quinone can not be polymerized. This is why the catechol in the solution of pH = 10.12 can not be polymerized electrochemically. Curve 6 shows the spectrum of a catechol solution with pH = 8.72 stored for 4 h, Even its absorbance is higher than the freshly prepared solution (Curve 5), no absorption peak is formed. Thus catechol in this situation can still be polymerized electrochemically.

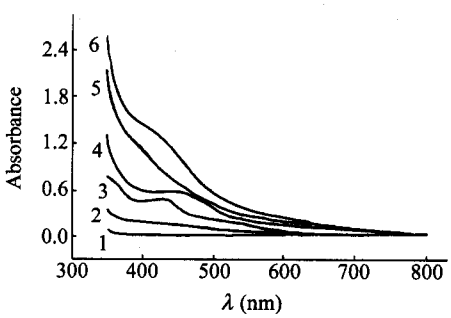


Fig. 3 UV-visible spectra curves: (1) pH = 1.03, (2) pH = 6.88, (3) quinone, (4) pH = 10.12, (5) pH = 8.72, (6) pH = 8.72 stored for 4 h.

The absorbance of the spectrum increases with increasing pH value from 1.03 to 10.12. This change is similar to that the peak currents of both the disk and ring electrodes at potentials less than 0.6 V increases with increasing pH value as shown in Fig. 2. These changes are related to the intermediate. The formation of the intermediates accelerates the oxidation of catechol. The anodic peak current at 0.33 V at pH = 10.12 is the largest among the above testing pH values. Also, its corresponding cathodic peak current is very large (Plot D in Fig. 2). This indicates that catechol was easily oxidized chemically to *o*-quinone by oxygen in air. The absorption peak at 449 nm (Curve 4 in Fig. 3) is mainly attributed to *o*-quinone.

Effect of rotation rate

The electrolytic solution used is the same as that shown in Fig. 1. The ring potential was set at −0.1 V. The potential scan rate was controlled at 50 mV/s. The rotation rate of the RRDE was 500, 1000, 2000, 2500 and 3000 r/min, respectively. Plots A and B in Fig. 4 show the results from the rotation rate at 500 and 1000 r/min, respectively. Comparison of Plot A and Plot B in Fig. 4 shows that both the disk current and the ring current increase simultaneously with increasing rotation rate. Based on two anodic current peaks on i_d-E curves and the corresponding cathodic currents on i_r-t curves, the ratios of i_r to i_d for the first scan were calculated. Fig. 5 shows the

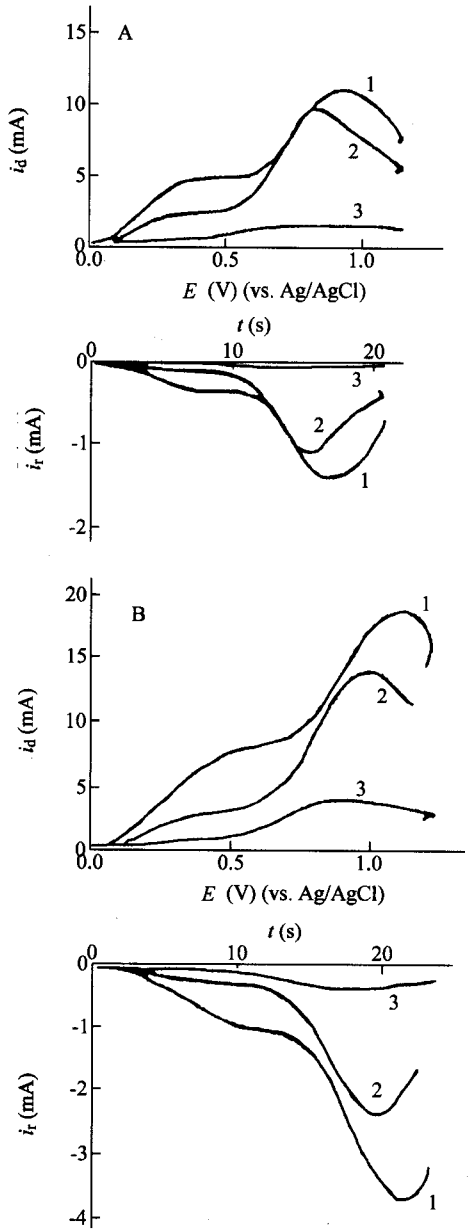


Fig. 4 Effect of rotation rate. The electrolytic solution is the same as Fig. 1, pH = 8.72, ring potential is set at −0.1 V. Potential scan rate: 50 mV/s. Plots: (A) 500 r/min, (B) 1000 r/min. Curves: (1) first scan, (2) second scan, (3) third scan.

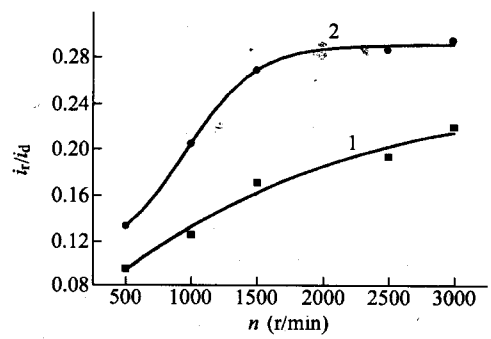


Fig. 5 Relationship between the ratio of i_r to i_d and rotation rate based on the data from the effect of the rotation rate on the peak currents. Curves: (1) 0.4 V, (2) 0.94 V.

relationship between the ratio of i_r to i_d and the rotation rate. Curve 1 is for the oxidation of catechol at 0.4 V, Curve 2 is for the polymerization of catechol at 0.94 V. It is clear that the ratio values of i_r to i_d for both kinds of intermediates increase with increasing the rotation rate. This indicates that some of intermediates generated at the disk were decomposed in their passage from disk to ring. So both intermediates in this case are not stable.

Effect of slow potential scan rate on the electrolysis

All above experiments were carried out at the potential scan rate of 50 mV/s. To understand whether the potential scan rate affects the electrolytic behavior of catechol at different rotation rates of the RRDE, the following experiments were performed at the potential scan rate of 5 mV/s and at the rotation rates of 500, 1000, 1500, 2000, 2500 and 3000 r/min. The electrolytic solution used is the same as that shown in Fig. 1. The pH value of the solution is 8.72. The ring potential is set at −0.10 V. Plots A, B and C in Fig. 6 show the experimental results of the RRDE at 500, 1500 and 2000 r/min. There are two oxidation peaks on i_d-E curve and two corresponding reduction peaks on i_r-t curve of each plot for the first scan. However, the disk current as well as the ring current is close to zero for the second scan. This indicates that catechol is more difficult to be polymerized further on the polycatechol film itself in this case.

Two oxidation peaks with about the same height occur on i_d-E curve and the corresponding reduction peaks also occur on i_r-t curve at the rotation rate of 500 r/min. Their peak potentials are at 0.27 and 0.93 V. From Fig. 6, it can be seen that the first oxidation peak potential is independent of the rotation rate and its peak current increases with increasing rotation rate. Based on the relationship between the peak current at 0.27 V and the rotation rate, the plot of the peak current i versus the square root of the rotation rate shows a straight line (omitted here). This indicates that the electrochemical oxidation of catechol at pH = 8.72 is controlled by mass transfer. This is to be expected. However, the second peak potential shifts to 0.77 V as the rotation rate increases from 500 to 2000 r/min and its peak current slightly decreases with increasing rotation rate. In fact, two small oxidation peaks at 0.77 and 0.93 V occur on the i_d-E curve (omitted here) at 1000 r/min, only the peak current at 0.77 V is a little lower than that at 0.93 V. The situation at 1500 r/min (Plot B) is just contrary to that at 1000 r/min, *i.e.*, the peak current at 0.77 V is a little higher than that at 0.93 V. As the rotation rate increases further, the peak at 0.93 V becomes smaller and smaller. Finally, this peak disappears at i_d-E curve as well as at i_r-t curve.

In Fig. 4 the anodic peak current at lower potential is less than that at higher potential, and both current peaks increase with increasing rotation rate. However, in Fig. 6 the anodic peak current at the lower potential is higher than that at the higher potential, and the anodic peak current at the higher potential decreases slightly with increasing rotation rate. This is caused by the potential scan rate. The time for passage from disk to ring is longer at the scan rate of 5 mV/s than that at 50 mV/s. Since the intermediates are not stable as mentioned above, the intermediates generated at the disk electrode during the oxidation of catechol at 0.27 V had been decomposed at a sufficiently high amount before polymerization, in the experiment with slow potential scan rate. As a result, the current of the anodic peak at the high potential is lower than that at the lower potential in Fig. 6.

ESR *spectrum of polycatechol*

Fig. 7 shows the ESR of polycatechol, which consists of a single line. Its g factor is 2.0079. The peak to peak line width ΔH_{P-P} is about 4 G, which is much larger than that of polyaniline.[16] It is clear that polycatechol possesses unpaired electrons.

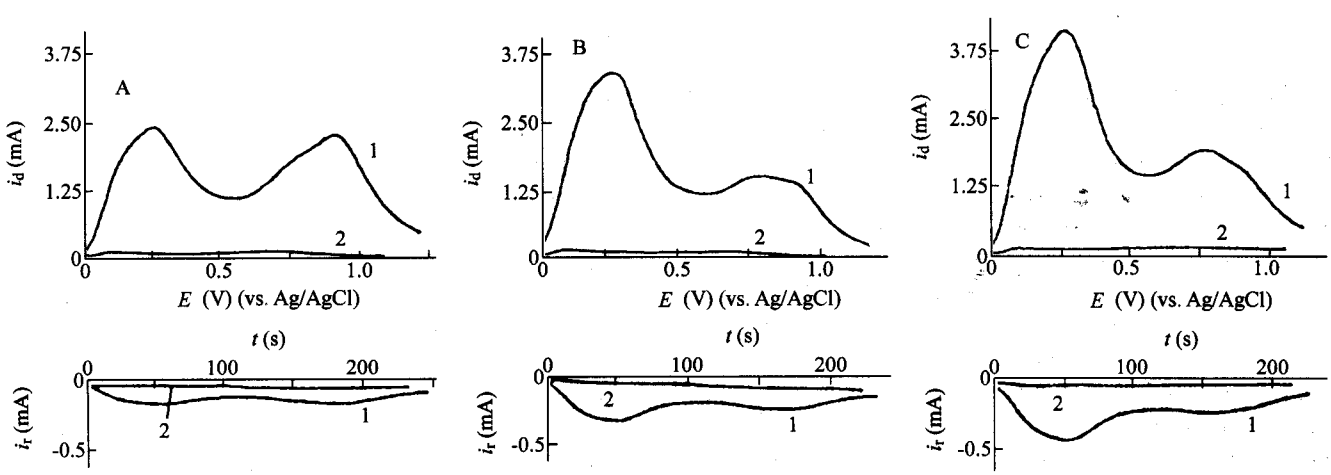


Fig. 6 Effect of the rotation rate on electrolysis at the potential scan rate of 5 mV/s. The solution is the same as Fig. 1. pH = 8.72. Ring potential is set at −0.1 V. Plots: (A) 500, (B) 1500, (C) 2000 r/min. Curves: (1) first scan, (2) second scan.

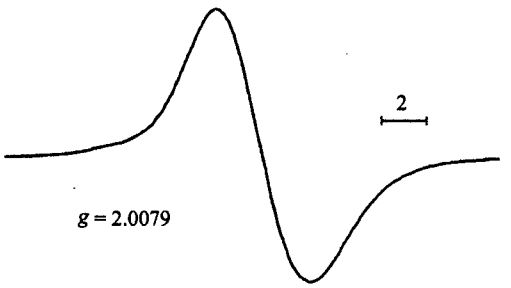


Fig. 7 ESR of polycatechol.

As mentioned previously, the intermediates produced during polymerization of catechol at about 0.4 and 0.9 V are the positively charged species. Thus these intermediates may be cation radicals. We found that no ESR signal was detected in the aqueous acidic solution of catechol, however an ESR signal was detected in the basic solution of catechol in the presence of alcohol (omitted here). This result is similar to the ESR signal of hydroquinone. But the ESR spectrum of catechol is different from that of hydroquinone. This is because all protons in the aromatic ring of hydroquinone are equivalent, however, four protons in the aromatic ring of catechol are at two different sites. Therefore, the electrochemical polymerization of catechol in the basic solution is likely to be carried out via the cation radicals.

Image of polycatechol films

As described above, the polymerization behavior of catechol under the potential scan rate of 50 mV/s is different from that of 5 mV/s , so which may influence the properties of polycatechol. To understand this question, following experiments were performed using cyclic voltammetry and scanning electronic microscope.

The polycatechol films used in the following experiments were prepared using repeated potential cycling between −0.2 and 1.1 V at different scan rates. The electrolytic solution consisted of aniline (0.2 mol/L), NaCl (0.5 mol/L) and Na_2HPO_4 (0.1 mol/L) with pH = 8.72.

The cyclic voltammetry of polycatechol was carried out in the solution of NaCl (0.5 mol/L) with pH = 1.0. The results show that the cyclic voltammogram of polycatechol synthesized using repeated potential cycling under the potential scan rate of 5 mV/s is identical in shape to that of the polycatechol synthesized under 50 mV/s. The latter cyclic voltammograms has been presented elsewhere.

Fig. 8(A) shows the image of polycatechol film obtained using repeated potential cycling for 5 cycles under the potential scan rate of 50 mV/s, which consists of granular particles with a diameter of 14—45 μm and some of short fibres. Fig. 8(B) shows the image of polycatechol film obtained using repeated potential cycling for 8 cycles under the potential scan rate of 5 mV/s, which consists of fibers with a diameter of 8—32 μm. So their morphology is different.

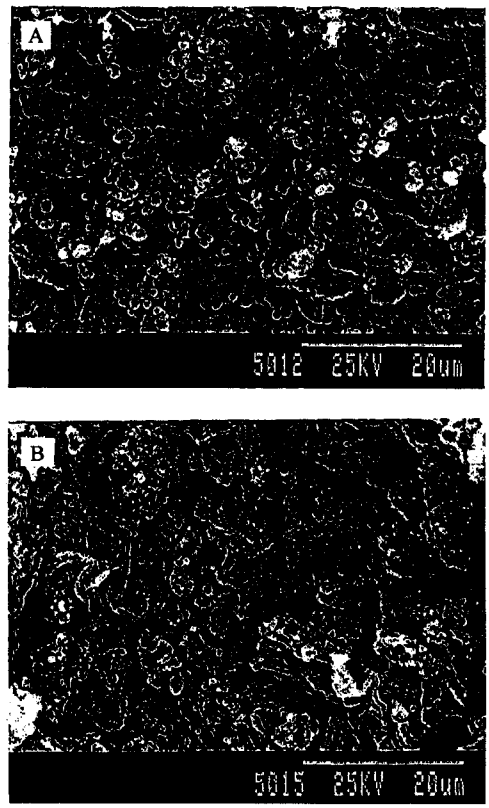


Fig. 8 Images of polycatechol films. Plots: (A) synthesized at the potential scan rate of 50 mV/s; (B) synthesized at the potential scan rate of 5 mV/s.

The above experimental results identify that the potential scan rate during electrolysis affects the image of polycatechol film, but does not affect the electrochemical property of polycatechol.

Conclusion

The electrochemical polymerization of catechol was studied using the RRDE under different ring potentials, rotation rates, potential scan rates and pH values, which provides wealth of information about the detection of intermediates, the ratio of i_r to i_d, shielding effect and mechanism of the electrode reaction. The results show that the electrochemical polymerization of catechol may be carried out via cation radicals.

At low pH values, the electrochemical polymerization of catechol is performed by one step. However, at higher pH values, the electrochemical polymerization of catechol was carried out by two steps. The first one is the oxidation of catechol and then followed by the electrochemical polymerization of catechol.

References

1 Bruno, F.; Pham, M, C.; Dubois, J. E. *Electrochim. Acta* **1977**, *22*, 451.

2 Pham, M. C.; Lacaze, P. C.; Dubois, J. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *86*, 147.
3 Mourcel, P.; Pham, M, C.; Lacaze, P. C.; Dubois, J. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *145*, 467.
4 Fleischmann, M.; Hill, I. R.; Mengoli, G.; Musiani, M. M. Akhavan, J. *Electrochim. Acta* **1983**, *28*, 1545.
5 Mengoli, G.; Musiani, M. M.; Furianetto, F. *J. Electrochem. Soc.* **1990**, *137*, 162.
6 Christie, I. M.; Vadgama, P.; Lioyd, S. *Anal. Chim. Acta* **1993**, *274*, 191.
7 Pariente, F.; Lorenzo, E.; Abruna, H. D. *Anal. Chem.* **1994**, *66*, 4337.
8 Pariente, F.; Lorenzo, E.; Tobalina, F.; Abruna, H. D. *Anal. Chem.* **1995**, *67*, 3936.
9 Davis, J.; Vaughan, D. H.; Cardosi, M. F. *Electrochim. Acta* **1997**, *43*, 291.
10 Sanchez-Cortes, S.; Francioso, O.; Garcia-Ramos, J. V.; Ciavatta, C.; Gessa, C. *Colloids and Surfaces A* **2001**, *176*, 177.
11 Chen, C. X.; Mu, S. L. *Chin. J. Poly. Sci.* **2002**, *20*, 309 (in Chinese).
12 Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, John Wiley & Sons, New York, **1980**, p. 302.
13 Shan, D.; Mu, S. L. *Electroanalysis* **2001**, *13*, 493.
14 Parker, V. D. *Electrochim. Acta* **1973**, *18*, 519.
15 Kong, Y.; Mu, S. L.; Mao, B. W. *Chin. J. Poly. Sci.* **2002**, *20*, 517 (in Chinese).
16 Mu, S. L. *Acta Phys.-Chim. Sin.* (*Wuli Huaxue Xuebao*) **1988**, *4*, 14 (in Chinese).

(E0112121 LU, Y. J.; LU, Z. S.)