

Articles

Electrochemical Behaviors of Hydroquinone on a Carbon Paste Electrode with Ionic Liquid as Binder

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In this paper the electrochemical behaviors of hydroquinone (H₂Q) were investigated on a carbon paste electrode using room temperature ionic liquid *N*-butylpyridinium hexafluorophosphate (BPPF₆) as binder (IL-CPE) and further applied to H₂Q determination. In pH 2.5 phosphate buffer solution (PBS), the electrochemical response of H₂Q was greatly improved on the IL-CPE with a pair of well-defined quasi-reversible redox peaks appeared, which was attributed to the electrocatalytic activity of IL-CPE to the H₂Q. The redox peak potentials were located at 0.340 V (E_{pa}) and 0.240 V (E_{pc}) (vs. the saturated calomel electrode, SCE), respectively. The formal potential (E⁰) was calculated as 0.290 V and the peak-to-peak separation (ΔE_p) was 0.100 V. The electrochemical parameters of H₂Q on the IL-CPE were further calculated by cyclic voltammetry. Under the selected conditions the anodic peak current was linear with H₂Q concentration over the range from 5.0×10^{-6} to 5.0×10^{-3} mol L⁻¹ with the detection limit as 2.5×10^{-6} mol L⁻¹ (3 σ) by cyclic voltammetry. The proposed method was successful applied to determination of H₂Q content in a synthetic wastewater sample without the interferences of commonly coexisting substances.

Key Words : Hydroquinone, Ionic liquid, Carbon paste electrode, Electrochemistry, Cyclic voltammetry

Introduction

Chemically modified electrode (CME) had been widely used in the field of electroanalysis due to its advantages such as lower costs, high sensitivity and good selectivity.¹⁻³ Different kinds of modifiers had been used to fabricate different types of CME with specific structures and functions. Recently room temperature ionic liquids (RTILs) had been used as a new kind of modifier for the CME. Due to the advantages of wider electrochemical window, higher ionic conductivity and good solubility, RTILs have the great potential applications in the field of electrochemistry and electroanalysis.⁴⁻⁶ Maleki *et al.* fabricated a novel carbon ionic liquid electrode by using a pyridinium-based ionic liquid as binder to replace paraffin, which not only provided a low background response but also showed enhanced high electrochemical performance.⁷ Dong *et al.* investigated the direct electrochemistry of enzyme in RTILs/carbon nanomaterials composite film modified electrode.⁸ Sun *et al.* constructed a 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) based carbon ionic liquid electrode and used it as the basal electrode to make a hemoglobin (Hb) modified electrode.⁹ The RTILs film modified electrodes were also used for the determination of dopamine (DA), uric acid (UA), chlorpromazine and nitric oxide (NO) *etc.*¹⁰⁻¹³ Zhao *et al.* also prepared a RTILs/carbon nanotube (CNT) composite film modified electrode for the voltammetric

determination of DA in the presence of UA and AA.¹⁴

Hydroquinone (H₂Q, 1,4-dihydroxybenzene) is an important substance in chemical industry with its many applications in the fields such as photographic developers, lithography, food antioxidants and the production of polymerization inhibitors for rubber. It is also commonly present in the environmental samples such as coast water, so it is necessary to establish a simple and sensitive method for H₂Q determination. Several analytical methods such as chromatography,¹⁵⁻¹⁷ electrochemistry^{18,19} and biosensors²⁰⁻²² *etc.* have been developed for the H₂Q determination in cosmetic creams and wastewater from photographic process.

In this paper the electrochemical behaviors of H₂Q were studied on a pyridinium-based ionic liquid modified carbon paste electrode (IL-CPE). In recent reports,^{7,23,24} IL-CPE had been demonstrated as a high-performance electrode with the advantages such as simple preparation procedure, wide potential windows, high rates of electron transfer and good anti-fouling ability. The experimental results indicated that H₂Q had an improved voltammetric response on IL-CPE compared with that on the CPE, which was due to the presence of ionic liquid on the electrode surface. The oxidation peak current had a good linear relationship with H₂Q concentration in the range from 5.0×10^{-6} to 5.0×10^{-3} mol L⁻¹. The proposed method had good ability to distinguish the coexisting catechol and successfully applied to the H₂Q determination in synthetic wastewater samples.

Experimental

Chemicals. Hydroquinone (H_2Q , Tianjin Basifu Chemical Limited Company), catechol (CC, Tianjin Kernel Chemical Limited Company), *N*-butylpyridinium hexafluorophosphate (BPPF₆, Hangzhou Kemer Chemical Limited Company), graphite powder (average particle size 30 μm , Shanghai Colloid Chemical Plant) were used without further treatment. Phosphate buffer solution (PBS) was prepared by mixing suitable amount of 0.1 mol L⁻¹ KH₂PO₄/Na₂HPO₄ and adjusted to the pH with 0.1 mol L⁻¹ H₃PO₄ or 0.1 mol L⁻¹ NaOH. Before experiments the working solution was deoxygenated with pure nitrogen for about 10 min and the electrochemical cell was kept in the nitrogen atmosphere during all the experiments. All the reagents used were of analytical reagent grade and the solutions were prepared by doubly distilled water.

Apparatus. A LK 98A electrochemical analyzer (Tianjin Lanlike Chemistry and Electron High Technology Company, China) was used for all the electrochemical measurements with a traditional three-electrode system. The room temperature ionic liquid modified carbon paste electrode (IL-CPE, $\Phi = 4.0$ mm) was used as the working electrode with a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The pH of PBS was measured by a pH-S-25 model pH meter (Shanghai Hongyi Instrumentation Company).

Procedure. The traditional carbon paste electrode (CPE) was prepared by hand-mixing of graphite powder with paraffin at a ratio of 70/30 (w/w) in an agate mortar. The homogeneous carbon paste was packed into a cavity of glass tube with the diameter of 4.0 mm. The electrical contact was provided with a copper wire connected to the paste in the end of tube. The procedure for the preparation of IL-CPE was carried out according to the reference,²⁵ which was made of graphite powder and BPPF₅ with a ratio of 3/1 (w/w). The surface of IL-CPE was carefully polished on a piece of weighing paper to get a mirror-like surface just before use.

Electrochemical investigation was carried out by cyclic voltammetry in a 0.1 mol L⁻¹ pH 2.5 PBS with the potential range from -0.2 to 0.8 V and the scan rate as 100 mV s⁻¹. All the measurements were carried out at room temperature.

Results and Discussion

Cyclic voltammogram of H_2Q . Figure 1 showed the cyclic voltammograms of H_2Q on traditional CPE (curve a) and IL-CPE (curve b) with the scan rate as 100 mV s⁻¹. On the CPE, a pair of small redox peaks appeared with the anodic peak potential (E_{pa}) as 0.452 V and the cathodic peak potential (E_{pc}) as 0.120 V (vs. SCE). The anodic (I_{pa}) and the cathodic (I_{pc}) peak current was got as -41.297 μA and 29.253 μA , respectively. The ratio of I_{pa}/I_{pc} was calculated as 1.41 and the peak-to-peak separation (ΔE_p) was got as 0.332 V. The formal peak potential (E^0), which is the midpoint of E_{pa} and E_{pc} , was obtained as 0.286 V (vs. SCE). The results indicated the electrode reaction was a

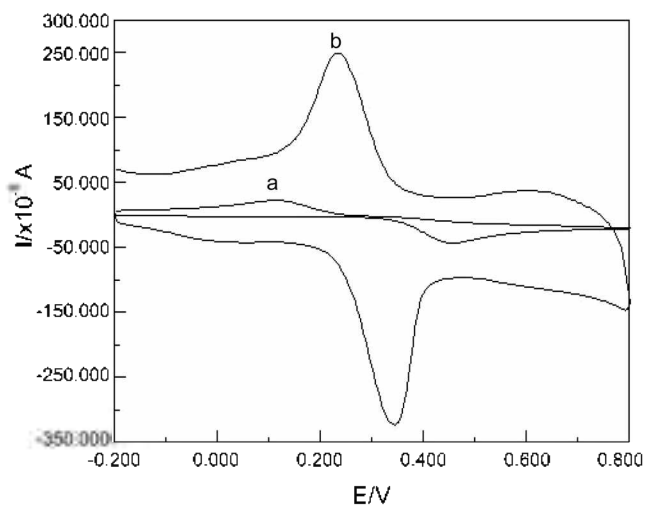


Figure 1. Cyclic voltammograms of 5.0×10^{-4} mol L⁻¹ H_2Q on CPE (a) and IL-CPE (b) in pH 2.5 PBS. Scan rate: 100 mV s⁻¹.

quasi-reversible process. While on the IL-CPE, the reversibility of H_2Q was significantly improved with the redox peak current increased greatly. From curve b it can be seen that the anodic peak potential was negatively shifted to 0.340 V and the cathodic peak potential was positively shifted to 0.240 V. The peak-to-peak separation (ΔE_p) was got as 0.100 V and the E^0 value as 0.290 V. The peak currents were about 7 folds larger than that on CPE with the ratio of I_{pa}/I_{pc} as 1.33. The small ΔE_p indicated that the overpotential of H_2Q at IL-CPE was remarkably lowered and the electrochemical reversibility of H_2Q on IL-CPE was much improved. At the same time the redox peak current was greatly increased. All the results was the indicative of a electrocatalytic reaction with faster electron transfer rates. ILs have the unique properties such as high conductivity, good solubility and high viscosity. When IL was mixed with graphite powder, it not only acted as a binder to bind the graphite powder together, but also filled into the void spaces

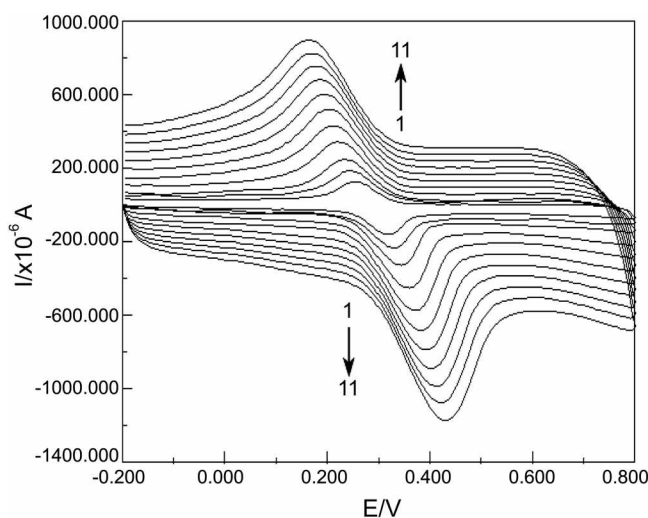


Figure 2. Cyclic voltammograms of 5.0×10^{-4} mol L⁻¹ H_2Q on IL-CPE with different scan rates in pH 2.5 PBS. (From 1 to 11: 30, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500 mV s⁻¹)

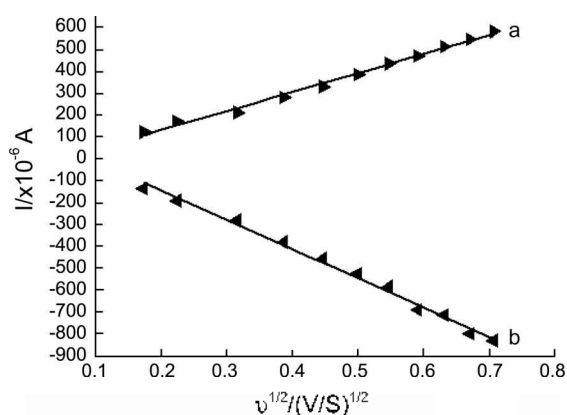


Figure 3. Plots of cathodic (a) and anodic (b) peak current with square root of the scan rate ($v^{1/2}$).

between the graphite powders to form an excellent charge-transfer bridge in the bulk of the CPE. A layer of IL was also formed on the surface of IL-CPE. So the significant improvement of the reversibility and sensitivity was achieved on the IL modified carbon paste electrode (IL-CPE).^{7,24}

Effect of scan rate. The influence of scan rate on the cyclic voltammetric response of H_2Q was carefully studied and the results were shown in Figure 2. It can be seen that with the increase of scan rate the redox peak current increased and the peak potential moved gradually.

In the scan rate from 30 to 500 $mV s^{-1}$ the redox peak current had good linear relationship with the square root of the scan rate ($v^{1/2}$) and the plot was shown in Figure 3. The results revealed that the electron process was a diffusion-controlled mechanism.

From Figure 2 it can also be seen that with the increase of scan rate the anodic peak potential was positively moved and the cathodic peak potential was negatively moved with the increase of the peak separation. The results indicated that the electron transfer rate was not very fast and the electrochemical reaction became less reversible. The relationship of redox peak potential with the $\ln v$ was constructed and the results were shown in Figure 4. According to the Laviron's equation²⁶ the charge transfer coefficient (α), the electron transfer number (n) and the electron transfer rate constant

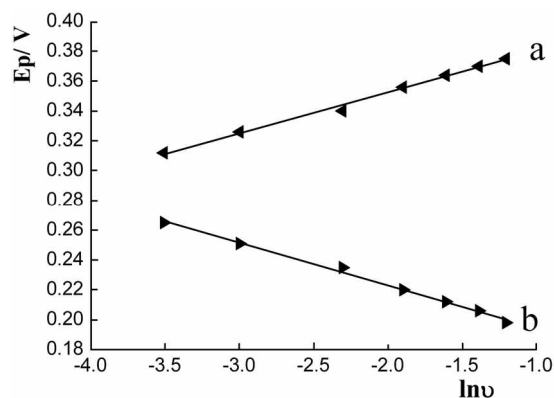


Figure 4. The relationship of the peak potential E_{pa} (a) and E_{pc} (b) against $\ln v$.

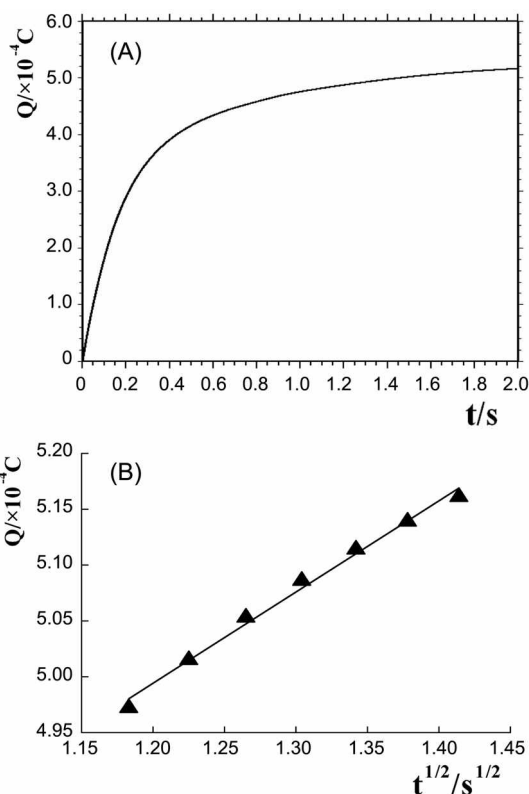


Figure 5. (A) Chronocoulometric curve of $5.0 \times 10^{-4} \text{ mol L}^{-1} H_2Q$; (B) The relationship of Q against $t^{1/2}$.

(k_s) were calculated as 0.51, 1.83 and 1.60 s^{-1} , respectively. The value of k_s was much larger than a previous reported value on CPE.²⁷ The result indicated that the IL-CPE showed enhanced electron transfer rate constant of H_2Q than that on CPE, which was mainly due to the presence of high conductive IL as the binder to promote the electron transfer rate.

Effect of buffer pH. The effect of buffer pH on the electrochemical response of H_2Q was investigated in the pH range from 2.0 to 9.0. The maximum anodic peak current appeared at pH 2.5, which was selected for H_2Q determination.

In the selected pH range the formal peak potential (E^0) also shifted negatively with the increase of solution pH. A linear regression equation between E^0 and pH was obtained as $E^0 \text{ (mV)} = -57.2 \text{ pH} + 428.2$ ($n = 9$, $\gamma = 0.997$). The value of slope was -57.2 mV/pH , which was close to the theoretical value of -59.0 mV/pH (25 °C). According to the equation:²⁸ $-59.0\alpha/n = -57.2$, the uptake of electron was accompanied by an equal number of hydrogen ion and $n = \alpha = 2$. The results indicated that two-electron transfer accompanied with two-proton transferred.

Chronocoulometric curve. Because the electrode process was controlled by diffusion, the diffusion coefficient (D) of H_2Q was further determined by chronocoulometric method. Figure 5A showed the chronocoulometric curve of $5.0 \times 10^{-4} \text{ mol L}^{-1} H_2Q$ and the relationship of Q with $t^{1/2}$ was plotted with the result shown in Figure 5B. According to the equation given by Anson:²⁹ $Q = 2nFAD^{1/2}Ct^{1/2}/\pi^{1/2} + Q_{dl} + Q_{ad}$. From the slope of the linear relationship between Q and

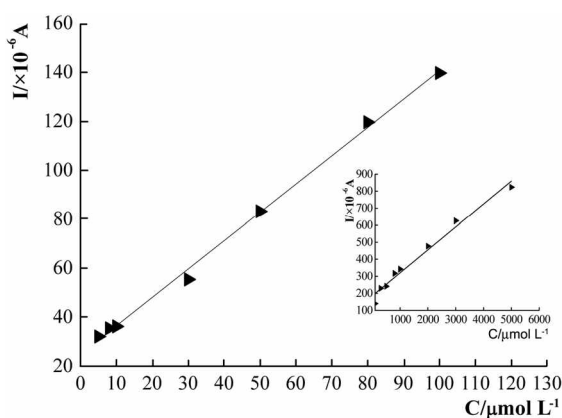


Figure 6. Calibration curve for H₂Q determination with IL-CPE.

$t^{1/2}$, the value of D was calculated as $7.88 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which was about 3.5 folds larger than a previous reported value of $2.26 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.³⁰ The result indicated that the electrochemical reaction was quickly on the IL-CPE.

Analytical characteristics. Under the selected conditions the oxidation peak current was increased with H₂Q concentration and the calibration curves were shown in Figure 6. The linear regression equations were got as $I_{pa}(\mu\text{A}) = -1.16C (\mu\text{mol L}^{-1}) - 25.07$ ($n = 7$, $\gamma = 0.999$) and $I_{pa}(\mu\text{A}) = -0.13C (\mu\text{mol L}^{-1}) - 185.45$ ($n = 8$, $\gamma = 0.990$) in the concentration range from 5.0×10^{-6} to $1.0 \times 10^{-4} \text{ mol L}^{-1}$ and 1.0×10^{-4} to $5.0 \times 10^{-3} \text{ mol L}^{-1}$, respectively. The detection limit was estimated to be $2.5 \times 10^{-6} \text{ mol L}^{-1}$ (3σ).

The reproducibility of the determination was performed with 20 successive determinations of $5.0 \times 10^{-4} \text{ mol L}^{-1}$ H₂Q. The relative standard deviation (RSD) was got as 2.9%, which indicated the proposed method showed good reproducibility. The IL-CPE can be stored for about 3 weeks without a decrease of the response to H₂Q, which showed good stability. Table 1 showed the comparison results of IL-CPE with other kinds of modified electrode for H₂Q detection. From the table it can be seen that this method provided comparable linear range and detection limit by cyclic voltammetry with the advantages such as simple preparation procedure.

Table 1. Comparison of different modified electrodes for H₂Q determination

Electrodes	Linear range	Detection limit	Method	References
	(mol L ⁻¹)	(mol L ⁻¹)		
MWCNT/GCE	$4.0 \times 10^{-7} - 1.0 \times 10^{-4}$	1.2×10^{-7}	DPV	3
ASP/GCE	$5.0 \times 10^{-6} - 6.0 \times 10^{-5}$	9.0×10^{-7}	DPV	31
P-Glu/GCE	$5.0 \times 10^{-6} - 8.0 \times 10^{-5}$	1.0×10^{-6}	DPV	32
MWCNT/GCE	$2.0 \times 10^{-6} - 1.0 \times 10^{-4}$	6.0×10^{-7}	LSV	33
MWCNT/GCE	$6.0 \times 10^{-6} - 1.0 \times 10^{-4}$	4.0×10^{-7}	DPV	34
L-Cys/Au	$2.0 \times 10^{-6} - 2.0 \times 10^{-4}$	4.0×10^{-7}	DPV	35
NG/GCE	$4.0 \times 10^{-6} - 3.2 \times 10^{-3}$	1.02×10^{-6}	CV	36
GCE	$3.0 \times 10^{-5} - 4.0 \times 10^{-3}$	2.0×10^{-5}	CV	This paper
IL-CPE	$5.0 \times 10^{-6} - 5.0 \times 10^{-3}$	2.5×10^{-6}	CV	This paper

MWCNT: Multiwall carbon nanotube, ASP: Aspartic acid, P-Glu: Poly(glutamic acid), L-Cys: L-Cysteine, NG: Nano-gold, DPV: Differential pulse voltammetry, LSV: Linear sweep voltammetry, CV: Cyclic voltammetry.

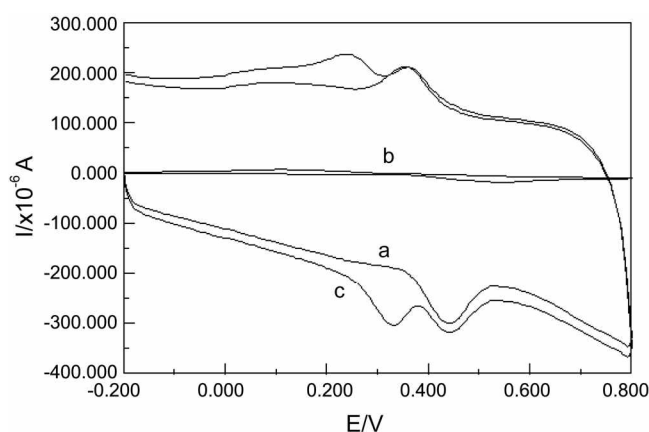


Figure 7. Cyclic voltammograms of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ CC on IL-CPE (a) and a mixed solution of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ CC and $1.0 \times 10^{-4} \text{ mol L}^{-1}$ H₂Q in pH 2.5 PBS on CPE (b) and IL-CPE (c). Scan rate: 100 mV s^{-1} .

Simultaneously determination of H₂Q and CC. H₂Q and CC are phenolic compounds and often coexist as isomers in the environmental samples. They have basic quinone

Table 2. Influence of coexisting substances on the determination of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ H₂Q ($n = 6$)

Coexisting substance	Concentration	Relative error (%)
Glucose	20.0 mg L^{-1}	-2.08
L-Glutamic acid	20.0 mg L^{-1}	-1.01
L-Cysteine	20.0 mg L^{-1}	-1.42
HSA	20.0 mg L^{-1}	-1.55
DNA	20.0 mg L^{-1}	-2.31
RNA	20.0 mg L^{-1}	-2.15
Na ⁻	$2.0 \times 10^{-2} \text{ mol L}^{-1}$	-1.30
Zn ²⁺	$2.0 \times 10^{-5} \text{ mol L}^{-1}$	-2.92
Ca ²⁺	$2.0 \times 10^{-5} \text{ mol L}^{-1}$	-1.83
Cu ²⁺	$2.0 \times 10^{-5} \text{ mol L}^{-1}$	-1.97
Mg ²⁺	$2.0 \times 10^{-5} \text{ mol L}^{-1}$	-0.93
Br ⁻	$2.0 \times 10^{-2} \text{ mol L}^{-1}$	-1.30

HSA: Human serum albumin, DNA: Deoxyribonucleic acid, RNA: Ribonucleic acid.

Table 3. Determination results of H₂Q in synthetic wastewater samples (n = 6)

Sample	Coexisting substances	H ₂ Q added (10 ⁻⁵ mol L ⁻¹)	H ₂ Q found (10 ⁻⁵ mol L ⁻¹)	RSD (%)	Recovery (%)
1	H ₂ Q, AA, Na ⁻ , Ca ²⁺ , Cu ²⁺ , Mg ²⁺ , Br ⁻	1.0	0.961	1.78	96.13
2	H ₂ Q, AA, Na ⁻ , Ca ²⁺ , Cu ²⁺ , Mg ²⁺ , Br ⁻	3.0	2.934	4.51	97.80
3	H ₂ Q, AA, Na ⁻ , Ca ²⁺ , Cu ²⁺ , Mg ²⁺ , Br ⁻	5.0	4.887	2.25	97.73
4	H ₂ Q, AA, Na ⁻ , Ca ²⁺ , Cu ²⁺ , Mg ²⁺ , Br ⁻	7.0	6.790	2.60	97.00

Conditions: H₂Q, AA (3.0 · 10⁻⁵ mol L⁻¹); Na⁻, Ca²⁺, Cu²⁺, Mg²⁺, Br⁻ (6.0 · 10⁻⁵ mol L⁻¹).

structure and can be electro-oxidated on the electrode. Simultaneous determination of H₂Q and CC level is of great necessary for their coexistence as isomers and highly toxic pollutants in environmental samples. So it is important to establish a precise method for the simultaneous determination of them without the previous separation procedure. Different kinds of modified electrode^{3,30,31} had been devised for the simultaneous investigation of H₂Q and CC. In this paper IL-CPE also showed excellent ability to separate the electrochemical responses of H₂Q and CC. Figure 7 showed cyclic voltammograms of H₂Q and CC in the mixed solution. It can be seen that on the IL-CPE CC exhibited a pair of redox peaks with E_{pa} as 0.436 V and E_{pc} as 0.356 V (curve a). While in the mixture solution of CC and H₂Q only a pair of redox peaks could be observed (curve b) on the traditional CPE with E_{pa} = 0.540 V and E_{pc} = 0.116 V, which indicated that the electrochemical responses of CC and H₂Q were overlapped and could not be distinguished. By using IL-CPE, the oxidation peak potentials were located at 0.328 V and 0.440 V (vs. SCE) (curve c), which were corresponded to that of H₂Q and CC. The separation of oxidation peak potential was got as 112 mV. So the IL-CPE showed excellent ability to separate the electrochemical response of CC and H₂Q.

Influences of coexisting substances. The influences of various coexisting substances including glucose, amino acids, metal ions, etc. on the determination of 1.0 × 10⁻⁴ mol L⁻¹ H₂Q were further investigated and the results were listed in Table 2. It can be seen that few of them disturbed the determinations and the fabricated IL-CPE showed good selectivity.

Sample analysis. The synthetic wastewater samples, which consisted of H₂Q, ascorbic acid (AA) and common ions including Na⁻, Ca²⁺, Cu²⁺, Mg²⁺, Br⁻, etc. were determined by the proposed method. The results were listed in Table 3 and it can be seen that the quantitative recovery in the range of 96.13%-97.80% was obtained. Therefore this proposed method was reliable, practical and reproducible.

Conclusions

In this paper an ionic liquid BPPF₆ modified carbon paste electrode (IL-CPE) was used as the working electrode for the investigation of the electrochemical behaviors of H₂Q. A great decrease of the overpotential and the increase of the peak current was observed on the IL-CPE. The electrocatalytic activity of IL-CPE was attributed to the higher

ionic conductivity and inherent catalytic ability of ILs themselves, which resulted the fast electron transfer rate on IL-CPE. Under the optimal conditions, the oxidation peak current was in proportion to H₂Q concentration in the range from 5.0 × 10⁻⁶ to 5.0 × 10⁻³ mol L⁻¹ with the detection limit as 2.5 × 10⁻⁶ mol L⁻¹ (3σ). The IL-CPE showed good ability to separate the electrochemical responses of H₂Q and CC in the mixed solution. The presence of coexisting substances showed no interferences to the determination and the established method was successfully applied to the H₂Q detection in synthetic wastewater samples.

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