



## Electrochemical Behaviour and Simultaneous Determination of Hydroquinone and Catechol at Poly-L-leu Modified Carbon Electrode

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Received: 8 February 2014;

Accepted: 21 May 2014;

Published online: 4 February 2015;

AJC-16762

The electrochemical redox reaction of hydroquinone and poly catechol was investigated with poly(L-leucine acid) modified glassy-carbon electrode (poly-L-leu/GCE) *via* cyclic voltammetry. The poly-L-leu/GCE has shown an excellent electrocatalytic activity for hydroquinone and catechol and two oxidation peaks of hydroquinone can be completely separated at this modified electrode. A highly selective and simultaneous determination of hydroquinone and catechol has been explored at the poly-L-leu/GCE. Under the optimized conditions, the differential pulse voltammetry response of the modified electrode to catechol and hydroquinone shows a linear concentration range of  $8 \times 10^{-6}$  to  $1.6 \times 10^{-4}$  mol/L with a correlation coefficient of 0.998 (or 0.994) and the calculated limit of detection is  $4 \times 10^{-6}$  mol/L at a signal-to-noise ratio of 3. The modified electrode in simulated water samples for the determination of hydroquinone and catechol have satisfactory results and recoveries were 97.3-104.2 %.

**Keywords:** Poly-L-leu/GCE, Simultaneous determination catechol and hydroquinone, Electropolymerization.

### INTRODUCTION

Phenols is a very important raw materials and chemical, which have toxic and difficult to degradation to pollution of the environment. From the prevention of pollution and application, it is necessary to establish a way fast, convenient and accurate method of measuring its content currently, the main methods of polyphenols determination are spectrophotometry<sup>1</sup>, high performance liquid chromatography<sup>2</sup>, continuous centrifugal partition chromatography<sup>3</sup>, enzymatic method<sup>4,5</sup> and electrochemical method<sup>6,7</sup>. But, the disadvantages of these methods are the sample pretreatment, complicated operation and not facilitate on-site testing.

In the electrochemical method, the amino acid is a kind of modified materials. Its application has attracted researchers' attention in chemistry<sup>8,9</sup>. Amino-modified electrode has three-dimensional structure and offers many applications in the spatial potential field, the high concentration of reactive groups, which has its high concentration of reactive groups, larger the electrochemical response signal and electrochemical stability and other characteristics. However, electrochemical polymerization on the electrode surface modified has become an important way of functionalization of the electrode surface and in the field of electric analytical chemistry has been widely used<sup>10,11</sup>. This paper described that a poly-L-leu/GCE composite modified electrode fabricated by electrodeposition of L-leucine

modified glassy carbon electrode was used to simultaneous determination of catechol and hydroquinone.

### EXPERIMENTAL

L-leucine was obtained from Boyi Chemical Reagent Co., Ltd. (Chongqing, China), hydroquinone and other analytical chemicals were purchased from the Sinopharm Chemical Reagent Co. Ltd. China (0.10 mol/L phosphate buffered solution (PBS, NaOH-KH<sub>2</sub>PO<sub>4</sub>) was prepared in our laboratory.

**Preparation of poly-L-leu/GCE/CME modified electrode:** GCE ( $\Phi = 3$  mm) was polished on a wet metallographic sandpaper (size 1000) and then was sequentially polished with 0.3 and 0.05  $\mu$ m alumina/water slurry on a polishing cloth to a mirror-like finish, followed by sonication and then rinsed with distilled water.

The treated GCE was immersed in PBS buffer solution containing  $2.5 \times 10^{-3}$  mol/L L-leucine and subjected to cyclic voltammetry in the range of -0.6-2.5 V at a scan rate of 100 mV/s for 15 cycles. Then the poly-L-leu/GCE modified electrode was prepared and ready to used the determination of hydroquinone and catechol.

All electrochemical experiments were carried out at LK2005A electrochemical workstation. A conventional three-electrode system was used where glassy carbon electrode or poly-L-leu/GCE, a platinum wire and a Ag/AgCl electrode

were used as working, counter and reference electrodes, respectively. cyclic voltammetry and differential pulse voltammetry were carried out in PBS (0.1 mol/L, pH=7) medium. Cyclic voltammetry was carried out on the electrolytic cell without stirring at a scan rate of 100 mV/s in a voltage range of -0.4 to 0.6 V. the potential increment is 9 mv, pulse amplitude is 5 mv, the pulse width is 0.5 s, pulse interval is 0.16 s by differential pulse voltammetry. All experiments were performed at room temperature 0.1 M PBS.

## RESULTS AND DISCUSSION

### Cyclic voltammetry curves of L-leucine polymerization:

Voltammograms of the poly-L-leu on the GCE are shown in Fig. 1. As can be seen from the Fig.1, a weak oxidation peak was observed with peak potential values at 1.3 V. The peaks' current increased upon continuous scanning, reflecting the continuous growth of the film of polymerization but the rate of increase reduced. These facts indicate that the poly-L-leu is deposited on the surface of GCE by electropolymerization.

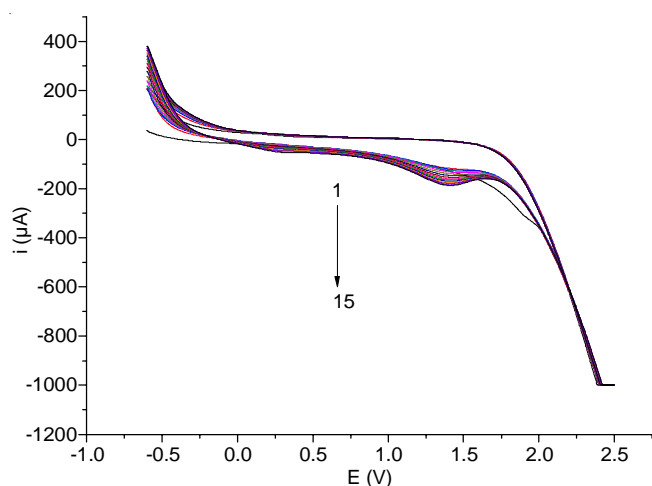


Fig. 1. Cyclic voltammogram of L-leucine acid in the polymerization process in 0.1 mol/L PBS (pH = 7) containing  $2.5 \times 10^{-3}$  mol/L poly-L-Leu. Scan rate: 0.1 V/S

**Voltammetric response of poly-L-leu/GCE to hydroquinone and catechol:** Cyclic voltammograms at poly-L-leu/GCE (curve 2) and bare GC electrode (curve 1) were also given from Fig. 2a. As can be seen, under the optimal conditions, At bare GCE, redox peaks of catechol was a relatively wide and its peak shape is poor. At poly-L-leu/GCE, redox peaks of catechol showed a relatively sharp and its redox peak currents increased significantly. It may be attributed to the higher surface area and strong adsorptive abilities of poly-L-leu film. Hydroquinone at bare GCE and poly-L-leu/GCE was also demonstrated a similar situation (Fig. 2b). All the results suggest that the poly-L-leu film modified carbon electrode greatly improves the sensitivity of determination of hydroquinone and catechol.

**Peak separation for dihydroxybenzene:** Cyclic voltammograms of catechol and hydroquinone under coexistence at poly-L-leu/GCE (curve 2) and bare GC (curve 1) electrode are shown in Fig. 3. As can be seen, the oxidation peaks of dihydroxybenzene could not be separated at the bare electrode and the oxidation peaks current is very small. Incontrast, at

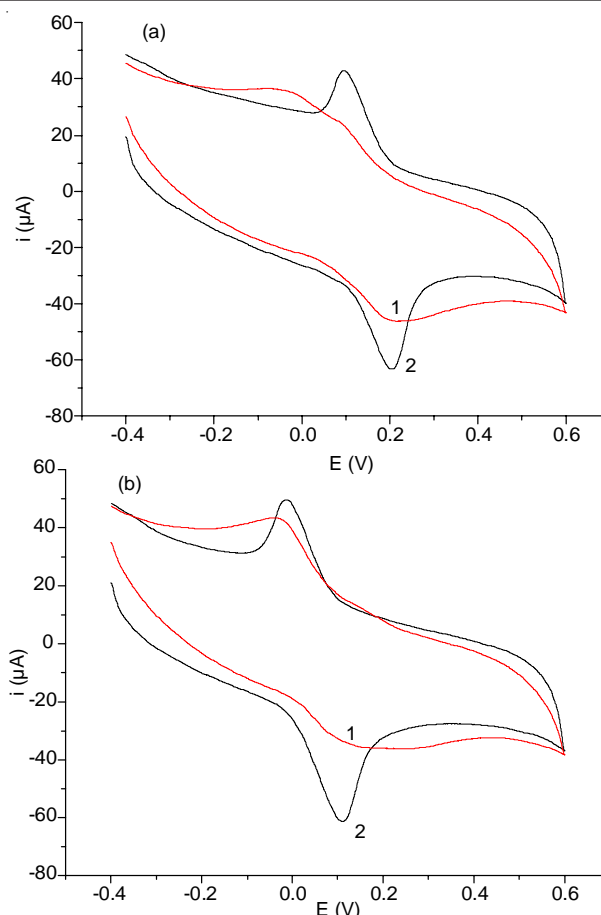


Fig. 2. Cyclic voltammograms of  $1 \times 10^{-4}$  mol/L catechol (a) and hydroquinone (b) in 0.10 M PBS (pH = 7) at the bare electrode (1) and at poly-L-leu/GCE (2) Scanning rate: 0.1 V/S

poly-L-leu/GCE, oxidation peak of dihydroxybenzene mixture at poly-L-leu/GCE showed two completely separated and currents reaches -60  $\mu$ A for hydroquinone and -64  $\mu$ A for catechol, which was significantly better than in the electrochemical response of GCE. This indicates that the modified electrode not only can effectively improve the electrochemical behaviour of catechol and hydroquinone, but also overlapped peaks in the GCE completely separated into two sensitive oxidation

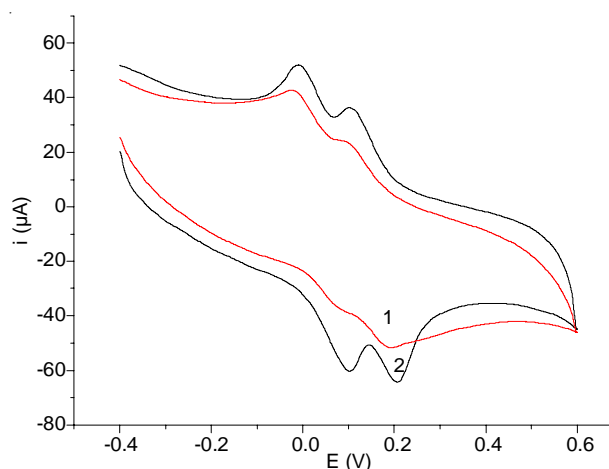


Fig. 3. Cyclic voltammograms for both catechol and hydroquinone in the mixed solution in 0.10 M PBS (pH=7) at the bare electrode (1) and at poly-L-leu/GCE (2). The concentrations of catechol and hydroquinone are both  $1 \times 10^{-4}$  M. Scan rate: 0.1 V/S

peak (potential difference 105 mv). Therefore, the modified electrode can be used for the simultaneous determination of catechol and hydroquinone.

**Effect of pH:** The pH (5.8-8) influence on the response of the sensor was carefully investigated in a series of in the presence of  $1 \times 10^{-4}$  mol/L hydroquinone and catechol mixed solution. As shown in Fig. 4, for hydroquinone and catechol, the response increased gradually from pH 5.8 to 7 and decreased from 7 to 8. but hydroquinone and catechol are no peak appears at Ph 8. So pH 7 was chosen as the optimum value for the analysis hydroquinone and catechol of simultaneous determination.

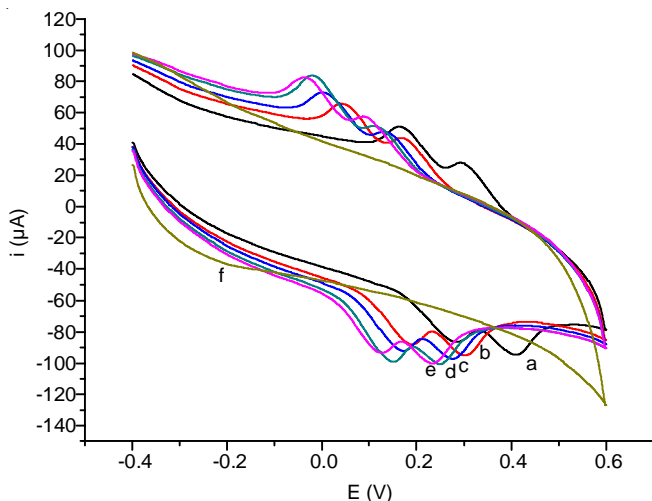


Fig. 4. Effect of pH on the direct electron transfer of  $1 \times 10^{-4}$  mol/L mixed solution of hydroquinone and catechol at poly-L-leu/GCE in 0.10 M PBS (pH=7). Scan rate: 0.1 V/S pH: a. 5.8; b. 6. 2; c. 6.6; d. 7.0; e. 7. 4; f.8.0 PBS

**Effect of scan rate on the electrochemical behavior of catechol and hydroquinone:** Under the optimization conditions, the effect of scan rate on the electrochemical behavior of  $1 \times 10^{-4}$  mol/L hydroquinone and catechol mixed solution was also investigated by cyclic voltammetry. As can be seen in Fig. 5, all the redox peak currents of catechol and hydroquinone increase with increasing scan rate. The oxidation peak current ( $I_{pa}$ ) and reduction peak current ( $I_{pc}$ ) is proportional to one side of scan rate from 50 to 200 mv/s. The regression equations was  $I_{pa} (\mu A) = -19.79 - 0.577v (mv/s)$  for hydroquinone and  $I_{pa} (\mu A) = -14.91 - 0.554v (mv/s)$  for catechol, with a correlation coefficient of 0.998 and 0.998, respectively. The regression equations was  $I_{pc} (\mu A) = 14.63 + 0.268v (mv/s)$  for hydroquinone and  $I_{pc} (\mu A) = 19.46 + 0.421v (mv/s)$  for catechol, with a correlation coefficient of 0.997 and 0.995, respectively. Indicating that the electrode reaction of hydroquinone and catechol at P-THR/GCE was a typical adsorption-controlled process.

**Simultaneous determination of hydroquinone and catechol:** The performance of the present sensor was also evaluated using differential pulse voltammetry technique to detect different concentrations of hydroquinone and catechol under the optimization conditions. The linear regression equations for hydroquinone and catechol were expressed as  $I_{pa} (\mu A) = -0.019c - 1.993 (\mu mol/L)$ ,  $I_{pa} (\mu A) = -0.018c - 1.938 (\mu mol/L)$ , respectively. The linear ranges for hydroquinone

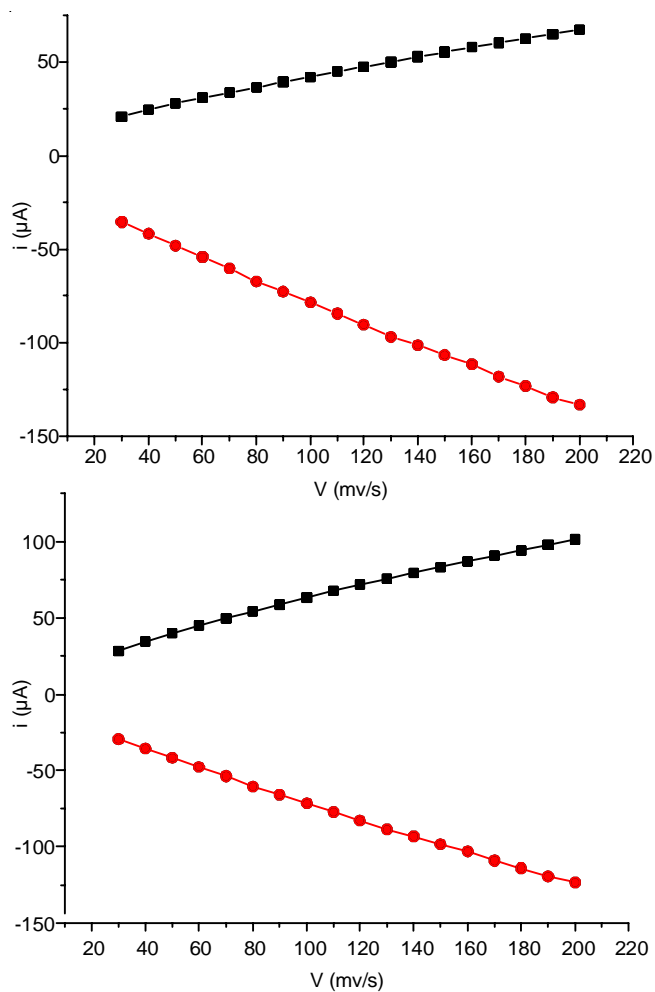


Fig. 5. Cyclic voltammogram of poly-L-leu/GCE containing both catechol and hydroquinone in the mixed solution in 0.10 M PBS (pH=7) with scan rate ranging from 30 to 200 as 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190 and 200 m v/s, respectively

and catechol both were found as  $8 \times 10^{-6}$ - $1.6 \times 10^{-4}$  mol/L and the detection limits (S/N = 3) both were  $2 \times 10^{-6}$  mol/L (Fig. 6).

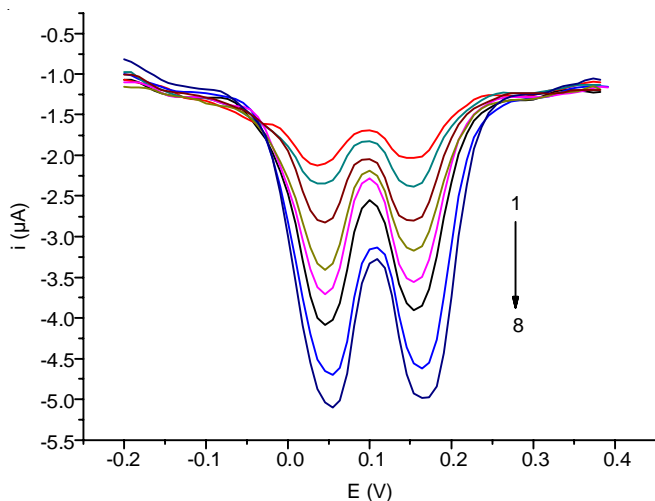


Fig. 6. Differential pulse voltammograms obtained at poly-L-leu/GCE in 0.1 mol/L PBS (pH=7) different concentrations mixed solution of catechol and hydroquinone: 8, 20, 40, 70, 90, 110, 160 and 160 µmol/L (from 1 to 8)

**Interference, reproducibility and stability:** The interference experiments on the determination of in the mixed solution containing  $4 \times 10^{-5}$  mol/L catechol and  $4 \times 10^{-5}$  mol/L hydroquinone at the poly-L-leu/GCE are examined. It is found that 100-fold excess concentrations of  $\text{Ag}^+$ ,  $\text{NO}_3^-$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{CO}_3^{2-}$ ,  $\text{I}^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{Cu}^{2+}$ , 2-fold excess concentrations of ascorbic acid, 20-fold excess concentrations of  $\text{Pb}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Br}^-$ , sucrose and 50-fold excess concentration of glutamic acid, glucose do not interfere (peak current change below 5 %). The results indicate that the intercalated this modified electrode has a good anti-interference ability.

Under optimized conditions, the same poly-L-leu/GCE were also investigated by measuring the response in the mixed solution containing  $1 \times 10^{-4}$  mol/L catechol and  $1 \times 10^{-4}$  mol/L hydroquinone. The relative standard deviation (RSD) for the oxidation peak current of catechol and hydroquinone in ten successive measurements was 2.8 and 2.5 %, respectively. And when the modified electrode was kept at 4 °C for 1 week, the peak currents retained more than 90 and 88 % of their initial values, respectively suggesting the good stability and reproducibility of the poly-L-leu/GCE

**Analytical application:** Under the optimal conditions, the poly-L-leu modified electrode was used for the detection of the mixed solution catechol and hydroquinone in artificial sewage samples (containing  $\text{Ag}^+$ ,  $\text{NO}_3^-$ ,  $\text{I}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Br}^-$  and  $\text{Na}^+$ ). The results obtained are also summarized in Table-1. As can be seen, quantitative recoveries of 97.3-104.2 % are obtained. This may imply the proposed modified electrode could be used to portably determine.

TABLE-1  
DETERMINATION RESULTS OF CATECHOL AND  
HYDROQUINONE IN WASTE WATER SAMPLES

Hydroquinone catechol					
Added ( $\mu\text{mol/L}$ )	Found ( $\mu\text{mol/L}$ )	Recovery (%)	Added ( $\mu\text{mol/L}$ )	Found ( $\mu\text{mol/L}$ )	Recovery (%)
20	20.32	101.6	20	20.24	101.2
40	41.44	103.6	40	42.52	106.3
80	78.86	98.57	80	77.98	97.5

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