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Electrocatalytic redox of hydroquinone by two forms of L-Proline

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Abstract

The redox behavior, the molecular mechanism and electronic transfer of hydroquinone interacted with two forms of L-Proline, covalent-linked to glass carbon electrode surface through C–N bond by electrooxidation and free dissolved in solution, were investigated by means of UV–vis and electrochemistry. The UV–vis spectrum showed that the reaction between free L-Proline and hydroquinone did not involve strong chemical bond. However, the electrochemical behavior of covalent-linked L-Proline is different from that of free one. Owing to electrostatic effect, the form of covalent-linked L-Proline favors electron transfer and enhances the reversibility of redox for hydroquinone. This phenomenon is conformed by cyclic voltammogram with a significant increase in peak current of hydroquinone redox and rate constant of electron transfer. It was found that it is a three-electron-transfer reaction. On the contrary, the form of free L-Proline unfavors electron transfer, resulting in a decrease in peak current of hydroquinone and rate constant, and the hydrogen bond was formed in the interaction.

Keywords: L-Proline; Hydroquinone; Covalent-modified; Electronic transfer; Electrocatalysis

1. Introduction

Hydroquinone is a high-volume chemical product used as a reducing agent, antioxidant, polymerization inhibitor, black-white film developer, anthraquinone dye, azo dyestuff and other chemical intermediate. It is also used in over-the-counter drugs as an ingredient in skin lighteners and is a natural ingredient in many agricultural and derived products, such as vegetables, fruits, grains, coffee, tea, beer and wine. As a pollutant, hydroquinone has negative effects for the health, it could enter into human body via skin, respiratory and digestive apparatus to erode skin and mucosa, and inhibit nerve center system. High concentration of hydroquinone can incur headache, fatigue, tachycardia, decompensation, the damage to kidney and even death. Long-term respiration in the atmosphere containing low concentration of hydroquinone can incur cough, dizzy, anorexia, nausea, spew and the pigmentation of the eye [1–5].

Electrolytic oxidation is an effective method to remove organic pollutants. But usually it is a high energy cost technique, due to high oxidation potential and low reduction potential for redox of pollutants. Therefore, the key task for electrolytic oxidation is to lower the oxidization potential or increase the reduction potential, so that reduce the energy cost.

Recently, the catalysis by biomolecules has been received considerable interest, in which enzyme catalysis is the most important issue [6–10]. In this paper, the electrocatalysis of L-Proline for the redox of hydroquinone was studied. It is known that amino acid is the basic unit of protein. The biofunction of protein is highly dependent on the properties of amino acids. So the investigation about the catalysis of amino acids for pollutant can provide a simple model for understanding the interaction between biomacromolecules and pollutants. L-Proline is a kind of natural N-substantial amino acids with structure of cyclopenta ring, and is osmoregulatory materials in cell with strong hydration ability [11]. In recently years, most investigations about L-Proline are focused on the relationship with osmosis of plants and application as chiral catalyst [12–16]. To the best of our knowledge, that the electrocatalysis of L-Proline to the redox of pollutants and the mechanism of electron transfer in the interactions between them are rarely reported.

In this paper, L-Proline was covalent-linked to glass carbon electrode (GCE) surface by electrooxidation through C–N bond. The different electrons transfer process between hydroquinone and two forms of L-Proline, covalent-linked and free dissolved in solution, was investigated by means of UV–vis and electrochemistry. The information about molecular orientation, reaction site

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and number of binding site during interactions were studied in detail.

2. Experimental

2.1. Covalent-linked L-Proline to GCE

The GCE (CHI Company, USA) was used as immobilized substrate of L-Proline. GCE was abraded with metallographic sand paper, then polished with alumina powder of 1.0, 0.3 and 0.05 μm, respectively. It was then sonicated in deionized water and ethanol bath for 5 min for each step to remove any residual alumina, and finally cleaned by cycling between 0 and +1.6 V versus saturated calomel electrode in H_2SO_4 solution of 0.5 mol L^{-1} at a scan rate of 100 mV s^{-1} until reproducible cycle was achieved.

The treated GCE was immersed in phosphate buffer solution containing L-Proline of 10 mmol L^{-1}, and subjected to cyclic voltammetry between −0.6 and +1.6 V at a sweep rate of 50 mV s^{-1} for 30 min, rinsed with buffer solution, washed with twice distilled water, and stored in dry nitrogen atmosphere, so the L-Proline/GCE was obtained.

The electrochemical behavior of thin layer of covalent-linked L-Proline was characterized by cyclic voltammetry in the phosphate buffer solution with electrolyte of $K_4Fe(CN)_6$ of 5 mmol L^{-1} and KCl of 0.1 mol L^{-1}. GCE with or without L-Proline was used as the working electrode; a platinum wire as the auxiliary and a saturated calomel electrode as the reference.

2.2. The electrochemical behavior of hydroquinone

The phosphate buffer solution of pH 6.86 containing hydroquinone of 1 mmol L^{-1} or solutions containing hydroquinone of 1 mmol L^{-1} and L-Proline of 1 mmol L^{-1} (or 2 mmol L^{-1}) was used as electrolytic solution. GCE with or without L-Proline were used as the working electrode. A saturated calomel electrode (SCE) was used as the reference electrode with a platinum wire as the counter electrode. The cyclic voltammetry was used to study the effect of L-Proline with different forms on the electrochemical behavior of hydroquinone.

The experiment was conducted with CHI660A (CH Instruments, USA) electrochemical workstation at room temperature. All solutions were bubbled with the ultra-pure nitrogen for 15 min to remove oxygen, and then kept in the nitrogen atmosphere during the measurements. The sweep rate was set at 100 mV s^{-1}. The potential mentioned in this paper was all relative to the potential of saturated calomel electrode.

2.3. UV–vis absorbance spectroscopy of interaction between L-Proline and hydroquinone

L-Proline of 2 mmol L^{-1} was added into hydroquinone of 1 mmol L^{-1}, then stirred, UV absorbance spectra of pure phenol solutions and mixed solutions were determined using Agilent 8453 UV–vis spectrophotometer.

3. Results and discussion

3.1. The electrochemical characterization of covalent modification of L-Proline on GCE surface

The cyclic voltammetric behaviors obtained on bare GCE and GCE with covalent-modified L-Proline in phosphate buffer solution are shown in Fig. 1. The background current was greatly decreased after L-Proline was covalent-linked to GCE surface owing to the formation of the thin layer. $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ is usually used as a probe to characterize the surface electrochemical property of an electrode. Fig. 2 is the cyclic voltammogram obtained on bare GCE and L-Proline/GCE in $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ solution. The background current was decreased in the case of modified GCE,

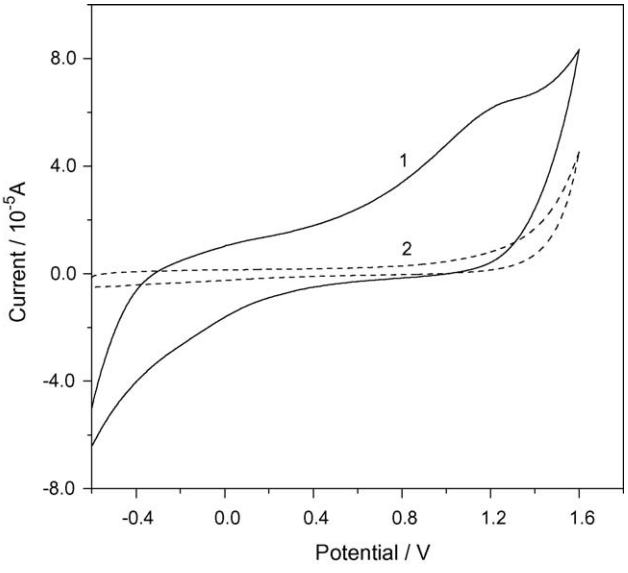


Fig. 1. Cyclic voltammograms of bare GCE and L-Proline/GCE in phosphate buffer solution: (1) bare GCE and (2) L-Proline/GCE.

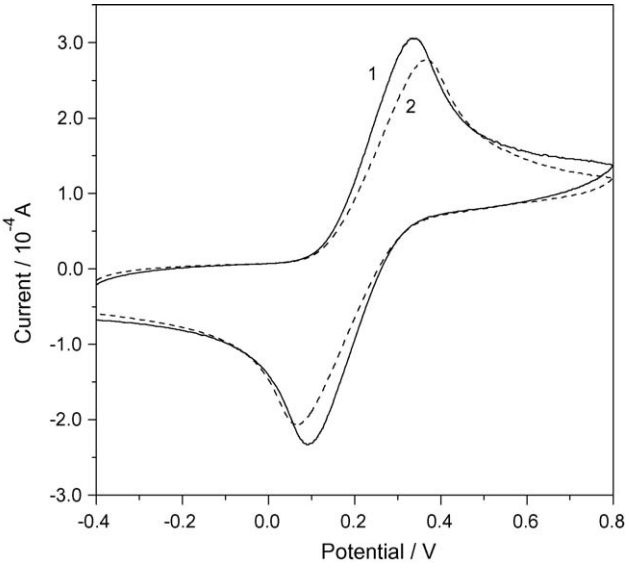


Fig. 2. Cyclic voltammograms of bare GCE and L-Proline/GCE in $K_4Fe(CN)_6$ solution: (1) bare GCE and (2) L-Proline/GCE.

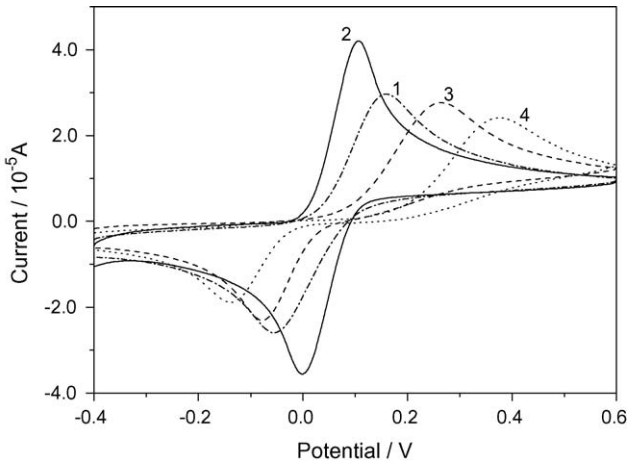


Fig. 3. The impact of L-Proline on the cyclic voltammograms of hydroquinone: (1) hydroquinone on bare GCE, (2) hydroquinone on L-Proline/GCE, (3) 1 mmol L^{-1} L-Proline + 1 mmol L^{-1} hydroquinone on bare GCE and (4) 2 mmol L^{-1} L-Proline + 1 mmol L^{-1} hydroquinone on bare GCE.

because electrostatic repulsion made hexacyanoferrate(III/IV) radicals difficult close to the surface of GCE, due to the negative charge of carboliylic in the end of L-Proline. Thus the redox reversibility of hexacyanoferrate(III/IV) was impaired and the current was decreased. This suggested that L-Proline immobilized on GCE surface formed a well-oriented and orderly arranged monolayer which baffles electrons transfer between electrolyte molecule and GCE [17].

3.2. Electrocatalytic redox of hydroquinone by L-Proline immobilized on GCE surface

The electrochemical behaviors of hydroquinone in case of two forms of L-Proline, covalent-linked to GCE surface and free dissolved in solution, were examined to obtain the information of molecular mechanism and electrons transfer process.

The voltammetric curves of catalytic redox of hydroquinone by L-Proline immobilized on GCE are shown in Fig. 3. A pair of redox peaks was observed for hydroquinone on bare GCE (curve 1). E_{pa} is about +0.160 V, E_{pc} about −0.056 V and the peak-to-peak separation ΔE_p is 0.216 V. A pair of redox peaks is also observed for the same concentration of hydroquinone on L-Proline-immobilized GCE (curve 2). But a negative shift for oxidation peak potential and a positive shift for reduction peak potential were observed. The peak-to-peak separation is decreased to 0.107 V. The redox reversibility was enhanced and the current peak was increased significantly. This indicated that catalytic reaction occurred between the immobilized L-Proline and hydroquinone. The catalytic reaction facilitates electron transfer between hydroquinone and electrode, as a result the redox of hydroquinone becomes easier.

3.3. Counteraction to the redox of hydroquinone by L-Proline freely dissolved in aqueous solution

The dependence of electrochemical behavior for hydroquinone on L-Proline, which was dissolved in solution and in the state of disorder, was further investigated. The voltammetric behavior of mixed solutions containing hydroquinone and L-Proline on bare GCE are shown in Fig. 3 (curve 4). The redox potential of hydroquinone is shifted when 2 mmol L^{-1} L-Proline was added into 1 mmol L^{-1} hydroquinone solution. The oxidation peak potential of hydroquinone is positively shifted to 0.376 V, while reduction peak potential is negatively shifted to −0.138 V. It is obvious that the redox behavior of hydroquinone on GCE was changed because of the addition of L-Proline. In other words, although some interactions could take place, free dissolved L-Proline has a negative effect on the electron transfer, resulting in a weaker redox of hydroquinone on GCE.

3.4. Kinetics of electrode reaction for hydroquinone with L-Proline of two forms

Cyclic voltammograms of hydroquinone on bare GCE, L-Proline/GCE and mixed solution of hydroquinone and L-Proline on bare GCE were measured at different potential sweep rates as shown in Fig. 4. The oxidation peak current and reduction peak current increased with increasing sweep rate, meantime, the oxidation peak potential is positively shifted and the reduction peak potential is negatively shifted, indicating that the redox reversibility of hydroquinone was impaired with increasing sweep rate.

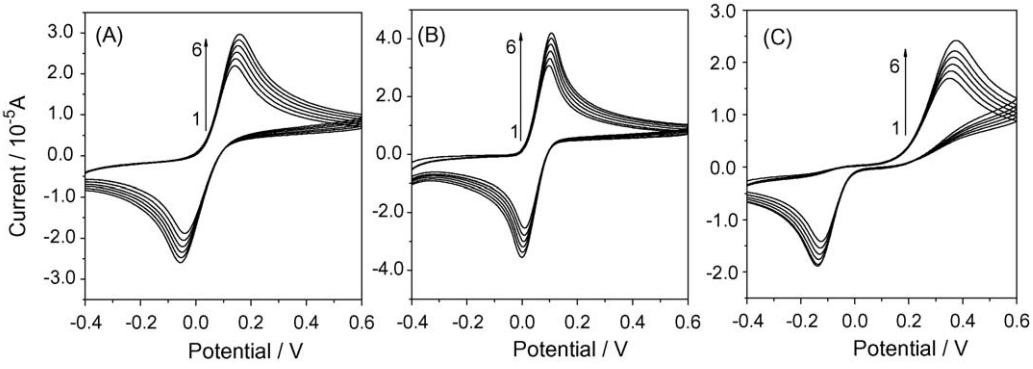


Fig. 4. Cyclic voltammograms of hydroquinone on GCE with different potential sweep rate: (A) 1 mmol L^{-1} hydroquinone on bare GCE, (B) 1 mmol L^{-1} hydroquinone on L-Proline/GCE and (C) 2 mmol L^{-1} L-Proline + 1 mmol L^{-1} hydroquinone on bare GCE. Sweep rate: (1) 0.05 V s^{-1}, (2) 0.06 V s^{-1}, (3) 0.07 V s^{-1}, (4) 0.08 V s^{-1}, (5) 0.09 V s^{-1} and (6) 0.1 V s^{-1}.

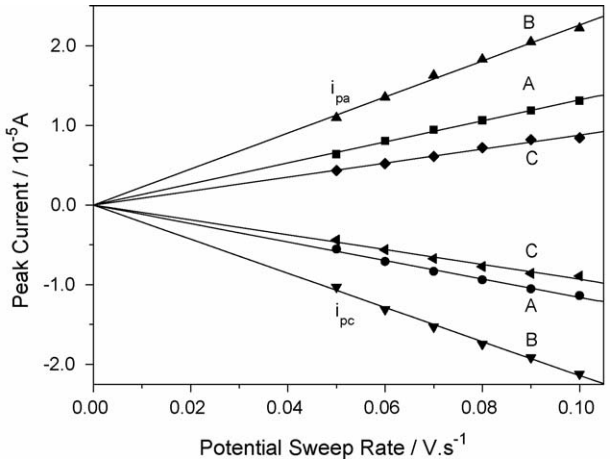


Fig. 5. The linear relationship between the magnitudes of redox peak current of hydroquinone on GCE and the sweep rate: (A) 1 mmol L^{-1} hydroquinone on bare GCE, (B) 1 mmol L^{-1} hydroquinone on L-Proline/GCE and (C) 2 mmol L^{-1} L-Proline + 1 mmol L^{-1} hydroquinone on bare GCE.

Fig. 5 shows that the magnitude of redox peak current of hydroquinone on bare GCE, L-Proline/GCE, and mixed solution of hydroquinone and L-Proline on bare GCE has linear relationship with the sweep rates; it indicates that the redox of hydroquinone on bare GCE and L-Proline covalent-modified GCE was a quasi-reversible surface reaction.

According to above results, the electron transfer kinetics of hydroquinone in the three different conditions can be obtained by using the approach developed by Laviron [18], when peak-to-peak separation is higher than 200 mV/n, the relationship between the peak potential E_p and the scan rate can be expressed in Eq. (1):

$$E_p = f(\lg \upsilon) \tag{1}$$

where for cathode peak, the slope value is $-2.3RT/\alpha nF$, and for anode peak, $2.3RT/(1-\alpha)nF$.

And k_s, the standard rate constant of reaction, is expressed in Eq. (2):

$$\lg k_s = \alpha \lg(1-\alpha) + (1-\alpha)\lg\alpha - \lg\left(\frac{RT}{nF\upsilon}\right) - \frac{\alpha(1-\alpha)nF\,\Delta E_p}{2.3RT} \tag{2}$$

where α is the transfer coefficient, n the number of electrons involved in the reaction and ΔE_p is the peak-to-peak separation. The resulting values of n, α and k_s are listed in Table 1.

Table 1
The electrode reaction parameters of hydroquinone

Hydroquinone	Number of electrons	Transfer coefficient	Standard rate constant (s^{-1})
On bare GCE	2	0.53	0.057
On L-Proline/GCE	3	0.46	0.41
Mixed solution on bare GCE	2	0.61	0.00017

The calculating results showed that the electrode reaction of hydroquinone on bare GCE was a two-electron-transfer step, the standard rate constant was 0.057 s^{-1}, and that on L-Proline covalent-modified GCE was a three-electron-transfer step and the standard rate constant 0.41 s^{-1}. However, when L-Proline and hydroquinone were dispersed in solutions, the electrode reaction of hydroquinone on bare GCE was still a process of two-electron transfer, and the standard rate constant was 0.00017 s^{-1}. It is an interesting result, indicating that the electrons transfer process of interactions between hydroquinone and two different state of L-Proline were different, thus their mechanism of redox were also different. The further discussion will be presented in the later section.

3.5. Molecular mechanism of interaction between hydroquinone and L-Proline

The molecular mechanism of interaction between hydroquinone and L-Proline was studied by means of UV–vis absorbance spectroscopy. The results are shown in Fig. 6. L-Proline has no absorption in the range of ultraviolet. However, hydroquinone has a strong absorption peak at 280nm, which is caused by $\pi \rightarrow \pi^*$ transition. Curves 2 and 3 are almost the same, indicating that the addition of L-Proline has no influence on the absorbance of hydroquinone. It might imply that neither cleavage of old chemical bond nor formation of new chemical bond occurred between hydroquinone and L-Proline.

Based on the electrochemical and UV absorption results, i.e., two different forms of L-Proline can interact with hydroquinone to cause the different electrochemical behavior and redox reaction; the interactions between L-Proline and hydroquinone is not strong chemical bond proved by UV–vis absorbance spectroscopy, the molecular mechanism of interactions between L-Proline and hydroquinone was assumed as follows.

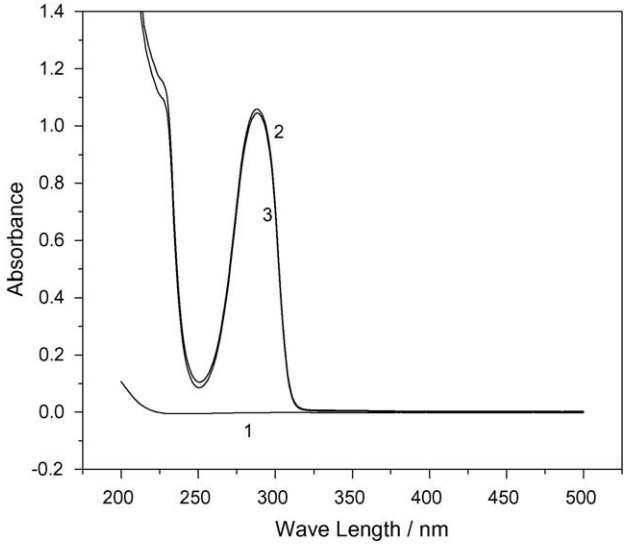
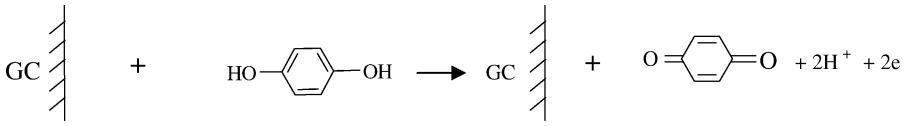
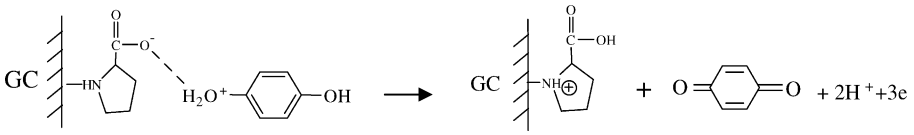


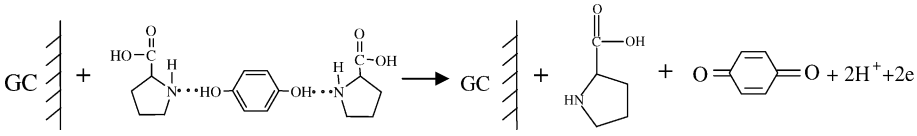
Fig. 6. UV–vis absorbance spectra of interaction between hydroquinone and L-Proline: (1) 2 mmol L^{-1} L-Proline, (2) 1 mmol L^{-1} hydroquinone and (3) 2 mmol L^{-1} L-Proline + 1 mmol L^{-1} hydroquinone.



Scheme 1. Electrons transfer mechanism of interactions between hydroquinone and L-Proline in hydroquinone on bare GCE.



Scheme 2. Electrons transfer mechanism of interactions between hydroquinone and L-Proline in hydroquinone on L-Proline/GCE. (—) Electrostatic force.



Scheme 3. Electrons transfer mechanism of interactions between hydroquinone and L-Proline in L-Proline + hydroquinone on bare GCE. (···) Hydrogen bond.

Due to the effect of oxidation, hydroquinone loses two electrons to become into benzoquinone. This process is a typical redox reaction, and the electrode reaction is shown in Scheme 1.

The isoelectric point of L-Proline is 6.30. In phosphate buffer solution of pH 6.86, the carboliylic group in L-Proline linked to GCE surface has negative charge, and hydroquinone is positive. Hydroquinone would be attracted by the negative L-Proline modified on GCE through electrostatic force, resulting in a decrease in distance between hydroquinone and electrode surface and an increase in concentration of hydroquinone near electrode surface. Thus, the redox reversibility of hydroquinone on GCE was enhanced and the peak current was greatly increased. On the other hand, the hydroquinone close to GCE surface also stimulates L-Proline to lose one electron and form L-Proline cation. As a result, the process is a three-electron transfer, the electron transfer mechanism is assumed as in Scheme 2.

When L-Proline and hydroquinone coexisted in solution, the process of electrode reaction is similar to that of hydroquinone on bare GCE, i.e., hydroquinone lost two electrons and became benzoquinone. However, under this condition, L-Proline would influence the electrode reaction activity energy of hydroquinone through intermolecular interactions. The nitrogen atom in the active group of –NH of L-Proline could be associated with oxygen atom in hydroquinone through N···H–O bond. One molecule of L-Proline has only one binding site while one molecule of hydroquinone has two hydroxyls. With the concentration of L-Proline increasing, the association formed between L-Proline and hydroquinone will turn from L-Proline·$C_6H_6O_2$ to (L-Proline)$_2$·$C_6H_6O_2$. Once the association of (L-Proline)$_2$·$C_6H_6O_2$ with relatively low energy has been formed, the energy needed during the process that hydroquinone was oxidized to lose two electrons and turned into benzoquinone would be increased because hydrogen bond must be overcome, so that the oxidation potential of hydroquinone increased and the reversibility of electrode reaction impaired. L-Proline in solution has a negative effect on the redox of hydroquinone and inhibits the electron transfer. The electrode reaction was showed in Scheme 3.

4. Conclusion

The redox behavior, molecular mechanism and electronic transfer process of hydroquinone interacted with two forms of L-Proline were investigated. The addition of L-Proline into hydroquinone solution did not change UV–vis spectrum of hydroquinone, indicating the interaction between two species is not strong chemical reaction. The effect of L-Proline covalent-linked to GCE surface on the electrochemical behavior of hydroquinone is absolutely different from that when L-Proline was freely dissolved in solution. L-Proline covalent-linked GCE through C–N bond by electrooxidation favors electronic transfer, resulting in a great increase in the redox peak current of hydroquinone, and the reaction is a process of three-electron transfer. But freely dispersed L-Proline has negative effect on the electronic transfer, thus causing a remarkable decrease in the redox peak current of hydroquinone; the reaction is a two-electron transfer process. This is due to the carboxyl acid group containing in the end site of L-Proline which covalent-linked to GCE was slightly negative in the buffer solution of pH 6.86, the electrostatic force between L-Proline and hydroquinone made hydroquinone closer to the surface of GCE, so that the oxidation of hydroquinone to benzoquinone become much easier. Meanwhile, the hydroquinone close to GCE surface stimulates L-Proline to lose one electron to form L-Proline cation. L-Proline dispersed in solution could be intermolecular coordinated with hydroquinone through hydrogen bond of N···H–O; as a result, the activation energy for the oxidation of hydroquinone is increased because an additional energy is needed to destroy hydrogen bond. The results of present investigation will be helpful to explore new biocatalytic strategies.

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