

Influence of acidity and auxiliary electrode reaction on the oxidation of epinephrine on the pre-anodized carbon paste electrode



Jing Li^a, Enbo Shangguan^{a,b,*}, Dan Guo^a, Fengli Gao^a, Quanmin Li^{a,*}, Xiao-Zi Yuan^c, Haijiang Wang^c

^a Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, PR China

^b Post-Doctoral Research Center of Henan Huanyu Group Co. Ltd., Xinxiang 453002, PR China

^c National Research Council of Canada, Vancouver, BC V6T 1W5, Canada

ARTICLE INFO

Article history:

Received 18 August 2015

Received in revised form 11 October 2015

Accepted 22 October 2015

Available online 29 October 2015

Keywords:

Pre-anodized carbon paste electrode

"U" shape electrolytic cell

Epinephrine

Cyclic voltammetry

ABSTRACT

In this paper, the influence mechanisms of the solution acidity and the auxiliary electrode reaction on the oxidation peak current of epinephrine (EP) were researched on a pre-anodized carbon paste electrode in a "U" shape electrolytic cell. By changing the solution acidity in the auxiliary electrode electrolytic cell (AEEC) or the working electrode electrolytic cell (WREEC), the electrochemical behaviors of EP in the WREEC was investigated by cyclic voltammetry. It is found that the magnitude of the oxidation peak current of EP is closely related to the solution acidity for both WREEC and AEEC. The effects of the supporting electrolyte, the reduction reaction at the auxiliary electrode, distribution of the EP species and the molecular configuration of EP on the oxidation peak current of EP were also explored. Furthermore, the reaction mechanisms for both cathode and anode were proposed and interpreted. With the provided electrode reaction mechanisms, optimized pH value can be chosen based on the distribution coefficients for future related researches. Satisfactory results have been achieved for the determination of EP in injection using these mechanisms.

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1. Introduction

Because of its versatility and convenience, cyclic voltammetry (CV) as an electroanalytical technique has been extensively studied and widely applied in the fields of electrochemistry, organic chemistry, inorganic chemistry, and biochemistry [1–6]. Nowadays, CV has been one of the most useful analytical techniques for the study of electroactive species [7–11]. It can be used to investigate the reversibility of electrode reaction and the adsorption of reactant or product in the process of electrode reaction, measure the standard electrode potential of a reversible system, and distinguish the reaction products of electrodes. Also, research of various electrode processes controlled by chemical reactions belongs to this domain [9–12]. As a consequence, CV is capable of rapidly observing the redox behavior of a compound, biological material, or an electrode surface over a wide potential range.

Generally, during CV testing, when the scanning speed and working electrode remain unchanged, the size of peak current depends on many factors, such as the scanning rate, the reacting species, the concentration of electrically active components, and acidity of the supporting electrolyte. As a result, various factors, which have an important influence on the size of peak current, are usually discussed and optimized in detail in the CV experiment [13–14]. In light of the Nernst equation, as the electrode reaction loses a proton, its oxidation potential always reduces with the increase in pH. This implies that the analytes can easily be oxidized at the working electrode and the oxidation current should increase accordingly along with the increment of pH. As a matter of fact, the oxidation peak current sometimes only increases with the raise of pH within a certain range. In other words, only in a definite range, this is consistent with the theoretical inference. When pH exceeds a specified value, although the oxidation peak potential shifts negatively with the increase in pH, the oxidation current decreases. This is inconsistent with the theory that the lower oxidation peak potential and the easier to be oxidized. So far, this phenomenon has not been given a specific explanation in the previous literatures [15–16].

* Corresponding authors. Tel.: +86 373 3326335; fax: +86 373 3326336.
E-mail addresses: shangguanbo@163.com (E. Shangguan),
mercury6068@hotmail.com (Q. Li).

In this context, we designed an experiment to study the effects of the solution acidity and the oxygen reduction reaction at the auxiliary electrode on the peak current. As is well known, the determination of epinephrine (EP) is very important for developing nerve physiology, pharmacological research and life science, which has attracted much attention of researchers [17–21]. Furthermore, the carbon paste electrode (CPE), which was firstly developed by Ralph N. Adams [22], nowadays has received increasing attention owing to its advantages of easy fabrication, low cost, lower background current, wide electrochemical window and ease of modification [23–28]. It was found that many oxygen-containing functional groups (such as carboxyl (—COOH), phenolic hydroxyl (—OH), lactones, and ethers) would be generated by means of a special pre-anodized treatment on the carbon surface of CPE [29]. An “electro-generated graphitic oxide (EGO)” film could then be formed on the carbon surface, which made the CPE demonstrate excellent electro-catalytic activities [29]. Based on the above considerations, we, in this work, observed the redox behaviors of the EP on a pre-anodized carbon pasted electrode.

In order to carry out the experiment conveniently, a “U” shape electrolytic cell (inner diameter 10 mm) (see Fig. 1) was constructed, in which a working electrode electrolytic cell (WEEC) and an auxiliary electrode electrolytic cell (AEEC) were separated from each other by a porous ceramics diaphragm at the bottom of the U-tube. A pre-anodized carbon paste electrode (PACPE) was prepared for the working electrode and a platinum wire was used as the auxiliary electrode. Both the working electrode and the reference electrode (SCE) were inserted in the WEEC of the “U” shape electrolytic cell, while the auxiliary electrode was inserted in the AEEC of the cell. By maintaining the acidity and concentration of supporting electrolytes in WEEC, the effect of different supporting electrolytes in AEEC on the oxidation peak current of epinephrine (EP) was investigated. The results demonstrate that the change of peak current is closely related to the solution acidity in both the WEEC and the AEEC. In addition, the effects of the

reduction reaction on the auxiliary electrode, and the effects of distribution for different species of EP and hydrogen bond catalysis on the oxidation peak current of EP are discussed in detail. In brief, this paper focuses on the influences of the acidity in the AEEC, distribution coefficients, as well as the degree of oxygen reduction reaction at the auxiliary electrode on the magnitude of peak current.

2. Experimental

2.1. Apparatus

CHI660C electrochemical workstation (Shanghai Chenhua Instrument Company, China) and a three-electrode electrochemical cell were employed; saturated calomel electrode (SCE) was prepared as the reference electrode; a platinum wire electrode was used as the auxiliary electrode; and a pre-anodized carbon paste electrode (PACPE) was served as the working electrode. A PFS-80 digital pH meter (Shanghai Dazhong Analysis Instrument Company, Shanghai, China) was used for the preparation of buffer solution. An ultrasonicator was utilized for cleaning (Kunshan ultrasonic instrument co., Ltd) and scanning electron microscope (SEM, JEOL JSM-7500F) was employed for observing morphology.

2.2. Reagents

$1.0 \times 10^{-2} \text{ mol L}^{-1}$ epinephrine (EP, Shanghai pure reagent Co. Ltd.) standard solution was prepared by accurately weighing 0.01831 g EP powder, then dissolved and diluted to 100 mL with HCl solution (1%V/V). The solution was kept in a refrigerator at 4 °C far from light. More dilute solutions were prepared with double distilled water. Graphite powder with a purity of 99.85% (Shanghai, China) and paraffin oil (C.P, Xinxiang, Henan) were used for preparing the PACPE. PBS buffer solution ($0.10 \text{ M NaH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$) with different pH values were prepared. $0.10 \text{ M H}_3\text{PO}_4$ and 0.10 M NaOH were used for adjusting the pH.

2.3. Preparation of PACPE

A proper amount of graphite powder was fully ground in the agate mortar, then mixed with graphite and paraffin oil (7:3, m/m) until a homogeneous paste was obtained. The mixture was packed into one end of a glass tube (5 mm internal diameter) and a copper wire was inserted into the carbon paste from the other end to provide electrical contact. When necessary, a new surface was refreshed by wiping an excess of the paste outside the tube and polishing it on a weighing paper. The electrode was then thoroughly rinsed with double distilled water and dried in the air.

The prepared carbon paste electrode (CPE) electrode was anodized by successive CV for 30 cycles from -0.3 V to $+1.5 \text{ V}$ with a scan rate of 100 mV s^{-1} in $0.2 \text{ mol L}^{-1} \text{ NaOH}$ solution. After pre-anodizing, the electrode was rinsed with double distilled water and dried at room temperature.

2.4. Experimental procedures

A certain volume of EP standard solution was transferred into the U-tube electrolytic cell with an inner diameter of 10 mm, as shown in Fig. 1, and diluted with buffer solution of PBS (pH = 7.00). The working-reference electrode was inserted in the WEEC of the U-tube electrolytic cell, and the auxiliary electrode in the AEEC, with both sides of the liquid level kept the same. The peak current of the EP was recorded at a scan rate of 100 mV s^{-1} between -0.3 V and $+1.5 \text{ V}$ by CV. All the experiments were accomplished at room temperature.

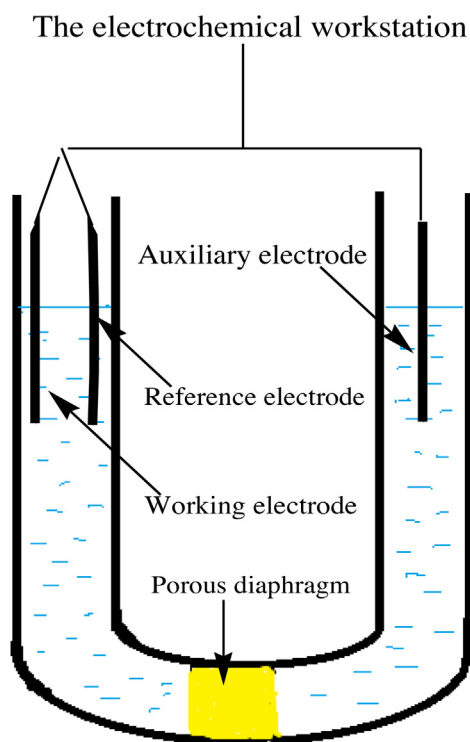


Fig. 1. The structure of the “U” shape electrolytic cell.

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