Journal of Electroanalytical Chemistry 823 (2018) 730–736

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Poly (glycine) modified carbon paste electrode for simultaneous determination of catechol and hydroquinone: A voltammetric study

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ARTICLE INFO

Keywords:
Electropolymerisation
Catechol
Hydroquinone
Glycine
Cyclic voltammetry

ABSTRACT

The poly (glycine) modified carbon paste electrode (MCPE) was fabricated for the determination of catechol and hydroquinone by cyclic voltammetric and differential pulse voltammetric techniques. The poly (glycine) MCPE exhibits high sensitivity and selectivity in the determination of catechol and hydroquinone in a binary mixture. The effect of scan rate was examined and it was found to be adsorption-controlled. The effect of concentration was studied in the range of 20-180 μM. The limit of detection (3S/M) and limit of quantification (10S/M) for CC were found to be 0.16 μM and 0.55 μM, respectively and for HQ the values were 0.20 μM and 0.66 μM, respectively. In order to show the selectivity of the electrode interference study was performed by varying the concentration of one analyte while keeping another analyte constant. Overall, a simple experimental procedure for fabricating the poly (glycine) MCPE was proposed with the merits of sensitivity, selectivity, reproducibility, and anti-fouling property towards the electroactive species and also in biological matrices.

1. Introduction

Phenolic compounds and its derivatives are important but toxic starting materials in a broad range of chemical manufacturing processes. Especially in coal conversion industry, phenolic residues are considered as an acute environmental problem [1]. Catechol (CC) (also known as pyrocatechol or 1,2-dihydroxy benzene) is an simple organic moiety, first discovered by destructive distillation of the plant extract catechin [2]. Small amounts of catechol occur naturally in fruits and vegetables. Upon mixing the enzyme with the substrate and exposure to oxygen (as when a potato or apple is cut and left out), the colorless catechol oxidizes to reddish-brown melanoid pigments, derivatives of benzoquinone. Benzoquinone is said to be antimicrobial, which slows the spoilage of wounded fruits and other plant parts. Catechol is produced by the reversible two-electron, two-proton reduction of 1,2-benzoquinone [3,4]. Hydroquinone (HQ) (1,4-dihydroxy benzene) is another phenolic compound coexisting with catechol in environmental samples. As an environmental pollutant it is toxic and can result in cancer like acute myeloid leukaemia [5]. High concentrations of HQ can incur headache, fatigue, tachycardia, decompensation, the damage to kidney, and even death. Long-term respiration in the atmosphere containing low concentrations of HQ can incur cough, anorexia, nausea, spew, and pigmentation of the eye. Even low concentrations of CC in foods and cigarette smokes may cause mutagenesis and cancerous alteration [6–8]. These two isomers are widely used in industrial products such as cosmetics, pesticides, flavouring agents. Very poor biological degradation in environment makes catechol and hydroquinone is harmful to humans, even in a minute concentration are the major causes for environmental pollution [9]. These two isomers are included as environmental pollutants in the lists of Environmental Protection Agency (EPA) and the European Union (EU) [10].

Several analytical methods have been reported for the simultaneous determination of these isomers such as spectrophotometry [11], chemiluminescence [12], HPLC [13]. However, these methods are generally expensive and time consuming. Because of the same phenolic moieties, overlapping of the peaks at same oxidation potential, co-existence and their competitive adsorption at the electrode surface makes the relationship between the voltammetric response of CC and HQ and their concentration in the mixtures nonlinear [14]. Therefore, it is important to establish a simple and fast analytical method for sensitive and selective determination of HQ and CC in different matrices. To overcome these limitations, electrochemical methods such as

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https://doi.org/10.1016/j.jelechem.2018.07.021
Received 27 November 2017; Received in revised form 11 July 2018; Accepted 13 July 2018

voltammetric one's were extensively used because of their simplicity in the experimental procedure, rapid and quick response, excellent reproducibility, good stability, low cost and low detection limit [15–17]. In the present scenario carbon paste electrodes became one of the most commonly used electrodes due to its simple preparation, low cost, easy renewability, good sensitivity, low background current and fast response [18,19]. However, the absence of conducting binder in the CPE will lower the sensitivity of the detection system. Many chemically modified electrodes were prepared for the simple and simultaneous determination of isomers such as poly (crystal violet) graphene modified carbon ionic liquid electrode [20], poly (brilliant blue) modified carbon paste electrode [21], poly (glutamic acid) glassy carbon electrode [22], poly(glycine) modified glassy carbon electrode [23].However, polymer modified electrodes (PMEs) have received great attention in recent years, as the polymer film which is deposited onto the surface of the electrode by electropolymerisation has good stability, reproducibility, more active reaction sites, homogeneity, and strong adherence to the electrode surface [24,25].

The present work describes an electropolymerisation of an amino acid say glycine on the surface of carbon paste electrode by cyclic voltammetry. The fabricated electrode has the capacity to resolve the voltammetric peaks of catechol and hydroquinone in a binary mixture. A simple method was reported for the determination of dihydroxy benzene isomers.

2. Experimental section

2.1. Apparatus and reagents

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed in an analytical system model CHI-660c potentiostat (Electrochemical workstation, USA). The conventional three electrode electrochemical cell contained a saturated calomel electrode (SCE) as a reference, platinum wire as a counter electrode and the working electrode was either bare CPE or poly(glycine) modified CPE. The pH values were measured with a digital pH meter MK VI (systronics). All the obtained oxidation potential values are given versus SCE.

Catechol (CC), hydroquinone (HQ) and glycine were purchased from Himedia. A stock solution of CC (25×10^{-4}M), HQ (25×10^{-4}M) and Glycine (25×10^{-3}M) were prepared in double demineralized water. Graphite powder (50 μm particle size) was purchased from Loba and silicon oil (as binder) was purchased from Himedia. All chemicals were of analytical grade. The chemicals for the preparation of buffer solution were purchased from Merck. The 0.2 M phosphate buffer solution (PBS) was prepared by mixing standard stock solutions of 0.2 M $NaH_2PO_4{\cdot}H_2O$ and 0.2 M Na_2HPO_4. All the solutions were freshly prepared prior to analysis. All the other solutions were prepared using double distilled water.

2.2. Preparation of working electrodes

The bare carbon paste electrode was prepared according to literature [19]. Electropolymerisation of glycine on the surface of carbon paste electrode was carried out by placing 1.0 mM glycine solution along with 0.2 M PBS of pH 7.0 in an electrochemical cell. The potential sweeping was maintained between −0.5 and +1.8 V at 0.1 V s^{-1} for 5 multiple cycles. Later the electrode was rinsed and washed with double distilled water prior to measurement.

3. Results and discussions

3.1. Optimisation condition for working electrode

The modification procedure for the preparation of working electrode was mentioned in the Section 3.2. From the Fig. 1, it can be seen that, the anodic peak current enhances gradually in the repetitive cyclic voltammograms. After the few cycles there is no increment in the peak height and it becomes more stable; which suggests polymerisation growth reached the saturation level [8,19,21].

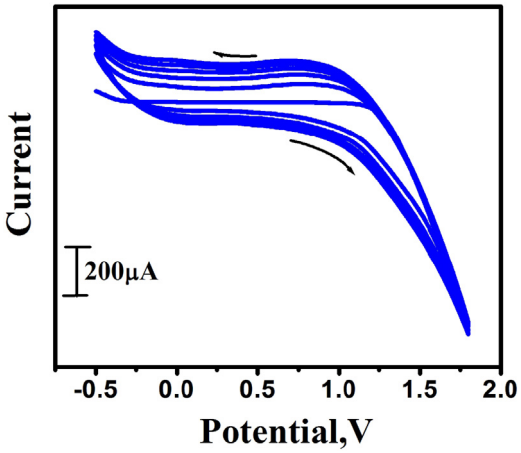
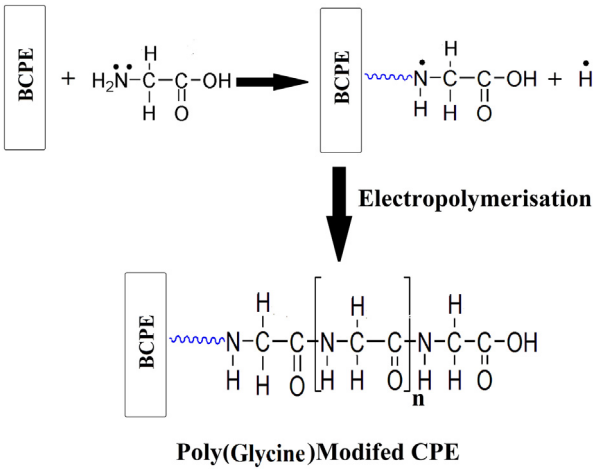


Fig. 1. Cyclic voltammograms of preparation of poly (glycine) modified CPE.1 mM aqueous solution of glycine was taken in 0.2 M PBS of pH 7.0 at 5 cycles with scan rate 0.1 V s^{-1}.

The extent of thickness of the polymer film has a significant influence on the electrocatalytic activity of the modified electrode. It is well known that, as the thickness of the modifier layer increases the electron transfer rate decreases due to insufficient exposure of reactive sites on the electrode. The thickness can be controlled by varying the cyclic voltammetry parameters. Therefore 5 repetitive cycles were fixed as an optimum for the fabrication of poly(glycine) modified CPE. The probable electropolymerisation mechanism of glycine is described in Scheme 1.

3.2. Electrochemical characterization of poly (glycine) modified CPE

In order to evaluate the performance of the poly (glycine) modified CPE, potassium ferrocyanide[$K_4Fe(CN)_6$] was selected as an electrochemical probe. Fig. 2 shows electrochemical response of 1.0 mM [$K_4Fe(CN)_6$] at bare CPE (dashed line) and poly(glycine) modified CPE (solid line) in 1 M KCl at the scan rate 0.1Vs^{-1}. A pair of redox peaks was observed for BCPE and with the modified CPE. The poly (glycine) MCPE shows lower peak potential difference (ΔEp), it was found to be 0.093 V and 0.101 V for bare and MCPE, respectively. As ΔEp is a function of electron transfer rate, lower the ΔEp means higher electron transfer rate. The result shows a dramatic change in the peak current at



Scheme 1. Probable electropolymerisation mechanism of glycine.