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Comparative investigation on electrochemical behavior of hydroquinone at carbon ionic liquid electrode, ionic liquid modified carbon paste electrode and carbon paste electrode

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Abstract

Ionic liquid, 1-heptyl-3-methylimidazolium hexafluorophosphate ($HMIMPF_6$), has been used to fabricate two new electrodes, carbon ionic liquid electrode (CILE) and ionic liquid modified carbon paste electrode (IL/CPE), using graphite powder mixed with $HMIMPF_6$ or the mixture of $HMIMPF_6$/paraffin liquid as the binder, respectively. The electrochemical behaviors of hydroquinone at the CILE, the IL/CPE and the CPE were investigated in phosphate buffer solution. At all these electrodes, hydroquinone showed a pair of redox peaks. The order of the current response and the standard rate constant of hydroquinone at these electrodes were as follows: CILE > IL/CPE > CPE, while the peak-to-peak potential separation was in an opposite sequence: CILE < IL/CPE < CPE. The results show the superiority of CILE to IL/CPE and CPE, and IL/CPE to CPE in terms of promoting electron transfer, improving reversibility and enhancing sensitivity. The CILE was chosen as working electrode to determine hydroquinone by differential pulse voltammetry, which can be used for sensitive, simple and rapid determination of hydroquinone in medicated skin cosmetic cream.

Keywords: Voltammetry; Ionic liquids; Carbon ionic liquid electrode; Ionic liquid modified carbon paste electrode; Hydroquinone

1. Introduction

The use of solid materials, such as composite electrodes, as detectors for electrochemical analysis is commonly known [1]. A composite electrode results from the combination of two or more materials. Carbon paste electrode is a type of composite electrodes prepared from graphite and organic liquid [2–7]. Generally, the organic liquid as a binder component of pastes is a non-conductive mineral oil, such as nujol, paraffin liquid or alike. However, there are two disadvantages of using mineral oil binder. One is that its component is not fixed and some unknown ingredients may yield unpredictable influences on detection and analysis. The other is that this binder is not conductive, which to some extent weakens the electrochemical response of CPE.

Ionic liquids (ILs) also known as a room temperature molten salts are characterized by melting point at or below room temperature [8]. In the past years, ILs have emerged as a frontier and novel area of research because of their unique chemical and physical properties, such as high chemical and thermal stability, almost negligible vapor pressure, high conductivity and wide electrochemical windows, etc. [9–16]. Recently, ILs have been proposed to be very interesting and efficient binders for the preparation of ILs-based paste electrodes [17–22]. Liu et al. [17] reported a CILE constructed by graphite powder mixed with ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) and the electrode increased the sensitivity of the response toward potassium ferricyanide. Maleki and coworkers [18,19] adopted a new strategy for the preparation of a novel CILE constructed by graphite powder mixed with ionic liquid *n*-octylpyridinum hexafluorophosphate (OPFP) as the binder, and stimultaneously determined dopamine, ascorbic acid and uric acid successfully. Li et al. [20] used the mixture of graphite powder-$BMIMPF_6$ paste as

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modifier coated on gold electrode for voltammetric determination of promethazine. Wang et al. [21] designed a carbon paste biosensors for the determination of H_2O_2 by entrapping heme proteins in carbon paste using $BMIMPF_6$ mixed with paraffin oil as a binder. Shul and coworkers [22] studied the ion transfer reaction across liquid|liquid interface at a CILE prepared with ionic liquid 1-decyl-3-methylimidazolum bis(trifluoromethylsulfonylimide) ($C_{10}MIMN(Tf)_2$) as binder. To our knowledge, there was no report about the fabrication of CILE and IL/CPE by using $HMIMPF_6$ as binder or modifier.

Hydroquinone has a simple and well-known oxidation mechanism and is commonly used in electrochemistry as a test analyte to validate new electro-analytical methods [23]. Hydroquinone and products containing hydroquinone have been widely used as depigmenting agents to lighten skin. However, because of the hazards of long-term treatments, the European Commission has banned the use of hydroquinone in cosmetics and it is available only through prescription by physicians and dermatologists [24,25]. Several analytical methods have been used for the determination of hydroquinone in samples of cosmetic creams. These include electrochemistry [25,26], high performance liquid chromatography [27,28], flow injection analysis [23,29], spectrophotometry [30,31] and biosensor [32]. Up to now, methods based on CILE and IL/CPE have not been reported for the study and determination of hydroquinone.

In the present work, two new electrodes, CILE and IL/CPE have been fabricated by $HMIMPF_6$. Potassium ferricyanide has been selected as a probe to evaluate the performance of the CILE, the IL/CPE and the CPE. The electrochemical response of hydroquinone at these electrodes in $0.1\,\mathrm{mol\,L^{-1}}$ phosphate buffer solution (PBS, pH 7.0) had also been investigated in detail and the electron transfer coefficient (α) and the standard rate constant (k_s) of hydroquinone at these electrodes were calculated, respectively. In addition, a novel method for the determination of hydroquinone with sensitive, simple and rapid characteristics was presented.

2. Experimental

2.1. Reagents and solution

Heptyl bromide (Shanghai Shiyan Reagent Corporation, Shanghai, China), ethyl acetate (Tianjin Chemical Reagent Corporation, Tianjin, China), hydroquinone (Chongqing East Chemical Reagent, Chongqing, China), potassium ferricyanide and potassium chloride (Xi'an Chemical Reagent Factory, Shaanxi, China) were of analytical reagent grade. The concentration of hexafluorophosphate acid is 65% (w/w) Hongyan Chemical Reagent Corporation, Jiangsu, China), and purity of 1-methylimidazole is 99% (w/w) Kaile Chemical Reagent Factory, Zhejiang, China). High purity graphite powder (Shanghai Carbon Plant, Shanghai, China) and paraffin liquid (AR, Kermel Center of Chemical Reagent, Tianjin, China) were used without further treatment. Other chemicals were all analytical grade. Ultrapure water (18.2 MΩ) was obtained from a Milli-Q water purification system and used throughout. Ionic liquid $HMIMPF_6$ was prepared following the similar procedures described in the literature [33,34].

Briefly, HMIMBr was prepared by the reaction of 1-methylimidazole with heptyl bromide (freshly distilled under reduced pressure) under vigorous stir at 70 °C for 72 h. Then the resulting viscous liquid was washed with ethyl acetate for three times and the remaining ethyl acetate was removed by heating under vacuum. The resulting viscous liquid was dissolved in ultrapure water, and HPF_6 in a 1.1:1 molar ratio was added dropwise into the mixture over 1 h under vigorous agitation. The mixture was stirred for 24 h at room temperature, then upper phase acidic aqueous layer was decanted and the lower $HMIMPF_6$ portion was washed with ultrapure water for many times, until the washings were no longer acidic. $HMIMPF_6$ was obtained by removing the remaining water under high vacuum. All experiments were under a dry nitrogen atmosphere.

$0.1\,\mathrm{mol\,L^{-1}}$ PBS (pH 7.0) was employed as supporting electrolyte. A $5.0\times10^{-3}\,\mathrm{mol\,L^{-1}}$ standard stock solution of hydroquinone was prepared daily in ultrapure water. Other solutions were prepared by appropriate dilution of the stock solution with ultrapure water. The determination of hydroquinone was performed on a medicated skin cosmetic cream purchased from local hospital.

2.2. Apparatus

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) experiments and electrochemical impedance measurements were performed on a CHI660A electrochemical workstation (Shanghai Chenhua Co., China) controlled by a microcomputer with CHI660 software. A three-electrode system was used, where a saturated calomel electrode (SCE) served as the reference electrode, a platinum wire electrode served as the auxiliary electrode and a CPE, a IL/CPE or a CILE served as the working electrode. All potentials reported were versus the SCE. In electrochemical impedance measurements, the applied perturbation amplitude was 0.005 V, the frequencies swept from 10^4 to 0.1 Hz, the number of points per frequency decade was 12 and initial potential was 0.17 V. DL-180 ultrasonic apparatus (Haitian Electronic Apparatus Company, Zhejiang, China) was applied in ultrasonic experiment. The surface morphologies of the prepared electrodes were observed through scanning electron microscopy (SEM) on JEOL JSM-6700F at an accelerating voltage of 20 kV.

2.3. Electrode Preparation

The CPE was prepared as follows: 1.0 g graphite powder and 0.5 mL paraffin liquid were mixed in a mortar by hand until a homogeneous paste was obtained. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and a cope wire was introduced into the other end for electrical contact. The preparation process of the CILE was similar to that of the CPE but a replacement of paraffin liquid with $HMIMPF_6$. A mixture of $HMIMPF_6$/paraffin liquid with ratio of 1/1 (v/v) was first ultrasonically dispersed for 5 min. Then the preparation process of the IL/CPE was same as the CPE, only replacing