

Original article

The selectivity of triethylene glycol modified glassy carbon electrode for charged and uncharged pieces

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ABSTRACT

A triethylene glycol modified glassy carbon electrode (TEG–GCE) was fabricated by a controlled-potential electrolysis procedure. The performance of the film on the modified electrode surface was investigated by cyclic voltammetry with different probes. It was firstly found that while neutral pieces could penetrate the TEG film on the GCE surface, the ionic pieces, whatever it is anion or cation, was blocked by the film. This property was successfully used for determining dopamine (DA) in the presence of ascorbic acid (AA) with differential pulse voltammetry (DPV).

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1. Introduction

Owing to its properties of high temperature resistance, extreme resistance to chemical attack and impermeability to gases and liquids, glassy carbon has been widely used as an electrode material in electrochemistry [1,2]. Based on glassy carbon electrode (GCE), various electrochemical sensors and biosensors have been fabricated by modifying the electrode with chemical or biological materials. The modification can change the electrocatalysis property, or improve the selectivity [3,4].

An electrochemical method for direct covalent modification of glassy carbon surfaces with 1-alkanol was proposed by Ohmori and co-workers [5–7]. They noticed that oxygen functionalities on the carbon surface increased when a carbon electrode was oxidized in an aqueous medium. They considered that the carbocations formed by the oxidation of the electrode reacted with water to create hydroxyl group sites on the electrode surface and some were further oxidized to carbonyl and carboxyl groups. Based on this consideration they proposed that alkoxy group could be immobilized on GCE surface by oxidizing the electrode in 1-alkanol medium. The alkanol molecules could be fixed on the electrode surface via an ether-linkage in this way. With the similar procedure, they also studied the properties of

GCE oxidized in α,ω -alkanediol and oligo (ethylene glycol) (OEG) medium, respectively [8–10]. Lin and co-worker reported a GCE covalently modified with poly(vinyl alcohol) by the similar procedure for simultaneous electroanalysis of dopamine, ascorbic acid and uric acid [11].

OEG is water soluble. OEG self-assembled monolayers have been widely used to prevent protein adsorption from biological media [12–14]. Ohmori and co-workers modified GCE with OEG by anodization of GCE in OEG, e.g. triethylene glycol (TEG) to eliminate protein adsorption, and applied the TEG modified GCE (TEG–GCE) in the electrochemical HPLC analysis of protein-containing samples [9,10]. In these studies, Ohmori and co-workers noticed that cationic and neutral pieces had good electrochemical performance on TEG–GCE while the electrochemical signal of anion was suppressed. They ascribed these phenomena to the anodization of the terminal hydroxyl groups to carboxylates on TEG–GCE surface.

However, we observed that cation was also blocked by the film on TEG–GCE surface. As far as we know, this property of TEG–GCE has not been noticed by other researchers. In this study, we first fabricated a TEG–GCE by an electrochemical oxidation procedure, and the performance of the film on electrode surface was investigated by cyclic voltammetry with different probes. As an application, the TEG–GCE was then used in detection of DA in the existence of ascorbic acid (AA) by differential pulse voltammetry (DPV) in neutral pH.

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2. Experimental

2.1. Reagents and apparatus

Dopamine hydrochloride (DA) and ascorbic acid (AA) were purchased from Wako Pure Chemicals (Osaka, Japan). Hexaamminecobalt(III) chloride, ruthenium hexaammine trichloride, potassium ferrocyanide, hexaamminecobalt(III) chloride, 3,4-dihydroxytoluene (DHT) and 3,4-dihydroxyphenylacetic acid (DOPAC) were all purchased from Sigma–Aldrich. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was purchased from Tianjin HengXing Chemical Reagent Co., Ltd. $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was obtained from Tianjin Damao Chemical Reagent Factory and $\text{FeNO}_3 \cdot 9\text{H}_2\text{O}$ was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. The reagents in different buffer solutions were prepared immediately before use. Buffer solutions were 0.1 mol/L KCl + 0.05 mol/L (citric acid + NaOH + HCl) buffer (pH 2.2), 0.05 mol/L KCl + 0.05 mol/L (citric acid + sodium citrate) buffer (pH 5.2), 0.1 mol/L phosphate buffer solution (PBS) (pH 7.2), 0.1 mol/L phosphate buffer solution + 0.05 mol/L NaOH (pH 9.2) and 0.05 mol/L $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ + 0.1 mol/L NaOH (pH 11.2). Triethylene glycol (TEG) was obtained from Nacalai Tesque INC. Glassy carbon (GC) disk was provided by Tokai Carbon Co., Ltd. The GCE was electrochemically modified by a potentiostat/galvanostat (HA301, Hokuto Denko, Tokyo, Japan) connected to a coulomb ampere hour meter (HF201, Hokuto Denko, Tokyo, Japan). Cyclic voltammetric experiments were performed at room temperature using an arbitrary function generator (HB105 Hokuto Denko) and a potentiostat/galvanostat (HA150). All differential pulse voltammetry (DPVs) and electrochemical impedance spectroscopy (EIS) measurements were performed with a CHI 660D electrochemical workstation (Chenhua, Shanghai, China). The electrochemical cell was assembled with a three-electrode system using a GC disk (with or without electrochemical modifications) as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as counter electrode.

2.2. Preparation of TEG–GCE

The cleaned GCE was subjected to controlled-potential electrolysis in TEG containing a supporting electrolyte (0.1 mol/kg LiClO_4) at 2.0 V [10]. The electric quantity flowing through the cell was controlled so as to control the deposition amount of TEG on GCE surface. Reference electrode was AgCl/Ag wire. After the treatment, the modified electrode was washed with water, MeOH and water, and then it was electrochemically treated in 0.1 mol/kg KCl solution by repetitively scanning the electrode potential between 0 and -0.5 V at rate 0.1 V/s for five cycles. After the electrochemical treatment, it was washed successively as the above steps. Then the modified electrode was ready for use.

3. Results and discussion

3.1. EIS characterization of the modified electrodes

Fig. 1 shows the Nyquist plots of the impedance spectroscopy of the bare and modified GCE. At a bare GCE, only a very small semicircle could be observed, showing a low charge transfer resistance (Fig. 1(a), $R_{ct} = 0.470$ k Ω). When TEG film was electrodeposited on GCE, the charge transfer resistance increased greatly (Fig. 1(b), $R_{ct} = 30.2$ k Ω), implying that the layer of TEG film obstructed charge transfer of the redox probe. As the increase of deposition electric quantity, the values of R_{ct} increased gradually (Fig. 1c–e). The results indicate that the TEG film inhibits the penetration of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox species toward the electrode, and this inhibition gradually strengthens with the increase of modifying electric quantity.

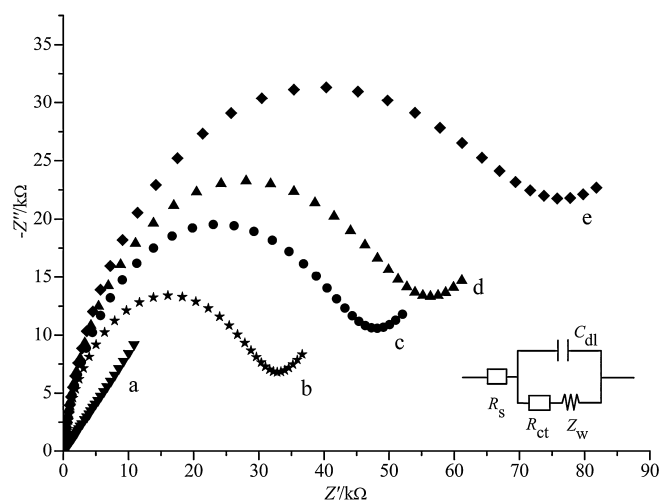


Fig. 1. Nyquist plot recorded in 5.0 mmol/L $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ containing 0.5 M KCl over a frequency range of 1.0×10^1 – 1.0×10^5 Hz on bare GCE (a), TEG–GCE with the electric quantity of 1.0 C (b), 3.0 C (c), 6.0 C (d), and 10.0 C (e).

3.2. Cyclic voltammetric response of TEG–GCE to ruthenium hexaammine and ferrocyanide

Ruthenium hexaammine trichloride and potassium ferrocyanide are hydrophilic inorganic compounds. Ruthenium hexaammine and ferrocyanide are positively and negatively charged respectively in PBS at pH 7.2, 5.2 and 2.2. Fig. 2(I) shows the cyclic voltammograms of 2 mmol/L ruthenium hexaammine trichloride solutions at pH 7.2, 5.2 and 2.2, respectively. Curve aa' shows the voltammogram on bare electrode, curves bb' and cc' show the voltammograms on GCE modified by TEG with electric quantity of 1.0 C and 3.0 C, respectively. As shown in Fig. 2(I), the voltammetric response of ruthenium hexaammine on bare electrode was almost reversible. However, the voltammetric response of ruthenium hexaammine on the electrode, which was treated in TEG with the electric quantity above 3.0 C, was almost completely blocked by the modified surface film.

Fig. 2(II) A, B, and C show the cyclic voltammograms of 2 mmol/L potassium ferrocyanide solution at pH 7.2, 5.2 and 2.2, respectively. Curve aa' shows the voltammogram of ferrocyanide on bare electrode, curves bb' and cc' show the voltammograms of ferrocyanide on GCE modified by TEG with electric quantity of 0.10 C and 1.0 C, respectively. The response of ferrocyanide on bare GCE was reversible, while it was completely blocked by the modified surface film when the electrode was modified by TEG with the electric quantity above 1.0 C.

The above results demonstrate that TEG film on GCE surface can suppress the response of analytes in water solution whether it is negatively or positively charged. In this case, the pH of the solution ranging from 7.2 to 2.2 had no significant influence on the electrochemical property of electrodes. These results were different from the reports [8,10], in which the authors proposed that the terminal hydroxyl group of TEG on GCE was oxidized to carboxyl group during the anodic modification, thus the TEG film was negatively charged at pH 7.2 and it just suppressed the response of anion, whereas cation had well response on the modified electrode.

To further confirm the resistance of TEG film to cation, cyclic voltammetric experiments of TEG–GCE to Cu^{2+} , Fe^{3+} , Fe^{2+} and hexaamminecobalt(III) were carried out at pH 7.2. The cyclic voltammetric responses of TEG–GCE to all of these cations were well blocked. (The figures are shown in supplementary data.) TEG–GCE showed a similar performance at higher pH than pH 7.2.

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