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Spontaneous adsorption and electrochemical behaviour of safranine O at electrochemically activated glassy carbon electrode

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ABSTRACT

The adsorption behaviour of safranine O (SO) at electrochemically pretreated glassy carbon electrodes has been studied. It was found that SO adsorption depended on the properties of the electrode surface, as determined by the nature and duration of the activation step. It was noticed that SO was adsorbed spontaneously and strongly on the surface of anodically pretreated electrode. The electrochemical behaviour of the modified electrode was investigated in H_2SO_4 (0.25 M) using cyclic voltammetry (CV). A reversible two electron, two proton wave was observed at −180 mV vs. SCE and the formal potential was found to be decreasing upon increasing the solution pH ($-56.8\,\mathrm{mV\,pH^{-1}}$). The modified electrode exhibited good stability on repeated scanning between −500 and 200 mV vs. SCE, causing only 5% decrease in the peak height after 100 cycles at a scan rate of $20\,\mathrm{mV\,s^{-1}}$. The surface coverage was calculated to be $0.812\,\mathrm{nmol\,cm^{-2}}$ and the electron transfer rate constant ($k_s^0 = 1.45\,\mathrm{s^{-1}}$) and transfer coefficient ($\alpha = 0.43$) for the adsorbed SO were evaluated using the Laviron method. The modified electrode clearly showed good electrocatalytic ability for oxygen reduction to H_2O_2.

1. Introduction

Glassy carbons GC are carbon materials prepared by pyrolysis of organic polymers and widely used in electroanalytical applications and electrode kinetics.

They exhibit several interesting features such as high chemical inertness, wide potential window which together with low porosity and low gas and liquid permeability [1,2] allow these materials to be very useful in electrode construction. In the past few decades, the modification of carbon surfaces has become of widespread interest to electrochemists, because of its application in electrocatalysis and chemical sensing. Numerous schemes for modifying electrode surfaces have been reported by several groups [3,4]. Amongst, spontaneous adsorptive attachment provides the most easy preparation procedure. Nevertheless, bare glassy carbons do not present a well-developed micro-porosity [2] and have been shown to be rather weak adsorbents for cations and neutral species [5]. However, it is well established in the literature that several kinds of activation procedures [6–16] can be efficiently applied to improve the adsorption characteristics of GC surfaces, such as ultrasonication [7], laser irradiation [9], carbon arc treatment [16]. Among these pretreatments, electrochemical activation is the most often used owing to its simplicity and good reproducibility [1,17]. The mechanism and surface changes induced by electrochemical activation were thoroughly discussed in the literature. Dekanski et al. [18] provided in their work some supporting evidence for the existence of highly ordered shells at the surface of bare GC electrode which can be easily removed by mechanical or electrochemical treatment, leading to its activation. Kepley and others [11,14,19,20] have suggested that electrochemical activation could increase oxygen-containing functional groups on the GC surface, leading to porous graphite layer responsible for the activation. This interpretation was recently confirmed by Zhao et al. [17].

Plain and electrochemically activated GC electrodes were extensively used for the preparation of modified devices, which were successfully applied for electrocatalysis and analytical estimation of various compounds [21–28]. During the past two decades, polyazines modified electrodes, obtained by anodic oxidation of phenazines, phenoxazines and phenothiazines, have attracted much research interest due to their good electron mediating and electrocatalytic properties [29–34]. As an example poly(phenosafranine) immobilized on GC electrode has been found to exhibit good electrocatalytic activity towards the oxidation of ascorbic acid in the presence of dopamine and serotonin [35]. On the other hand, Ganesan and Ramaraj [36] studied the reduction of oxygen on poly(phenosafranine) immobilized on a basal plane graphite (BPG) electrode and zeolite-L coated BPG electrode and reported that zeolite-L enhances the poly(phenosafranine) mediated oxygen reduction process at the modified electrodes. However, to the best our knowledge, nothing has appeared in the literature, neither on the adsorption of safranine O (Scheme 1) on bare or

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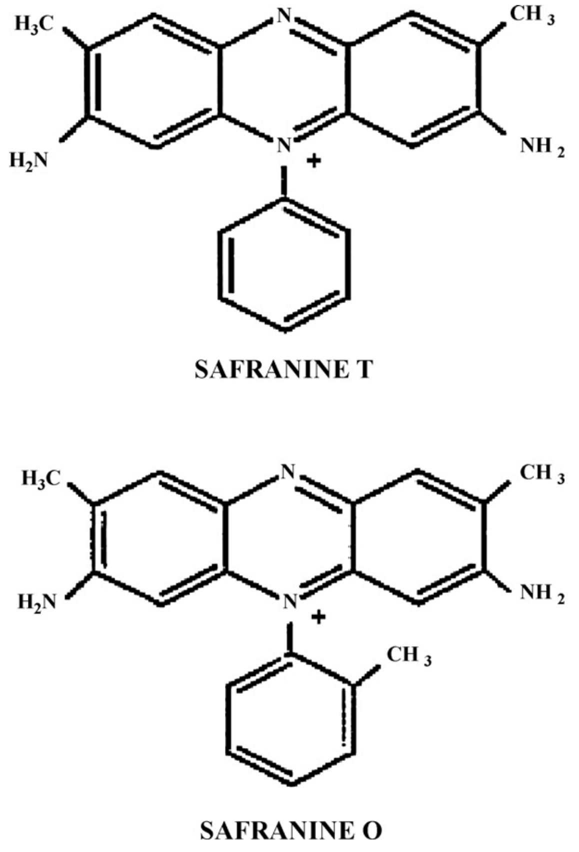

SAFRANINE T

SAFRANINE O

Scheme 1. Chemical structures of safranines.

activated GC electrode nor on the electrocatalytic activity of the modified electrode towards oxygen reduction.

The purpose of the present paper is to study the adsorption of SO on electrochemically activated GC. The effect of surface activation on the adsorptive attachment of SO was discussed and the stability of the modified electrode was evaluated. In addition, we investigated the electrochemical behaviour of the modified electrode and reported preliminary results showing the existence of a potent and persistent electrocatalytic activity towards the reduction of oxygen.

2. Experimental

2.1. Reagents

All chemicals used in this work were of analytical-reagent grade and used without further purification. Safranine O and sulphuric acid (98%) were purchased from (Fluka, France). All subsequent solutions were freshly prepared using doubly distilled ultra-pure water.

Impurity-free oxygen and nitrogen were used as outlined below. Before commencing electrochemical measurements, the electrolyte solutions were saturated with nitrogen. Before recording voltammograms in the presence of oxygen, the electrolyte solutions were saturated with oxygen.

2.2. Electrochemical equipments and procedures

All electrochemical measurements were performed in a single-compartment three-electrode glass cell, by using a Radiometer DEA 332 potentiostat, which was interfaced to a micro-computer running Voltamaster 2 software. A commercial saturated calomel electrode (SCE) was used as the reference and a platinum wire served as the auxiliary electrode. Bare and activated glassy carbon disks (diameter 5 mm) were used as working electrodes and prepared in the following manner. The electrodes were first hand polished with aqueous slurries of alumina (0.3 μm) on a felt pad for 5 min and then sonicated in acetone and double distilled water for 5 min.

Three methods were used to prepare the activated electrodes: the electrode referred as reduced glassy carbon (GC-red) was submitted to cathodic potential step at −1 V for 2 min in H_2SO_4 (0.25 M). The electrode referred to as oxidized glassy carbon (GC-ox) was anodized at 2 V versus SCE for 2 min GC-ox/red sample was obtained by exposing a freshly polished GC electrode to a 2 V anodic step for 2 min followed by a cathodic polarization step at −1 V for 2 min. All electrochemically activated electrodes were then briefly cycled between −0.5 and 1 V versus SCE, for five cycles at a sweep rate of 100 mV s^{-1} before being subjected to adsorption measurements. Following this, safranine modified electrodes were prepared using either of the above-mentioned electrodes (GC, GC-red, GC-ox, GC-ox/red). This consisted of immersing the working substrates in acidic safranine solution with stirring. The concentration and time of immersion were varied during experiments. Samples were then thoroughly washed with pure supporting electrolyte before subjected to electrochemical measurements.

The electrochemistry of the modified electrodes was examined in 0.25 M H_2SO_4 (pH = 1), except when exploring the pH effect. The solution's pHs were adjusted to the required values by appropriate addition of 1 M NaOH solution. The pH values were measured using a Mettler-Toledo 340 pH-meter.

3. Results and discussion

3.1. Physisorption of safranine O onto activated GC

3.1.1. Influence of the pretreatment on SO adsorption

The adsorptive attachment of safranine on glassy carbons was studied using cyclic voltammetry. Typical voltammograms obtained with bare and electrochemically activated GC electrodes, which were modified by dipping in 10^{-2} M solution of safranine for 20 min, are shown in Fig. 1. SO adsorption on the electrode surface is evidenced from the appearance of a pair of redox peaks, attributed to the reduction of adsorbed species and its oxidation on the return anodic scan. The voltammograms 1 and 2 obtained with GC and GC-red electrodes respectively are superimposed and nearly featureless within the working potential window, reflecting the absence of SO adsorption onto bare and exclusively reduced electrodes. In contrast, cyclic voltammograms of GC-ox and GC-ox/red exhibited a pair of intense and well-defined reversible peaks indicating the effective adsorption of SO on these electrodes. These findings are in agreement with results published by other groups [1,37–41] reporting effective adsorption of cations and neutral species on pre-anodized GC, while cathodic pretreatment did not lead to any activation of GC surface. This behaviour was attributed [1,11,17,19,20] to a substantial increase of oxygen-containing groups (phenolic, quinonic, carboxylic, etc.) on oxidized GC surface, leading to improved adsorption performance of the electrode. On the other hand, Ilangovan and Chandarasekara Pillai [42] observed measurable removal of O-containing groups on cathodisation. Dekanski et al. [1], based on Auger-electron spectroscopy and XPS measurements, have found that the cathodic pretreatment did not result in

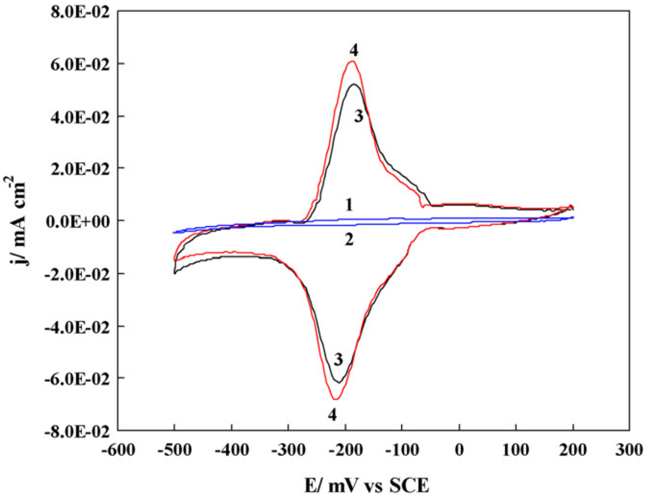

Fig. 1. Cyclic voltammograms of bare and activated GC electrodes, modified by immersion in 10^{-2} M solution of safranine for 20 min. (1) Bare GC electrode, (2) GC-red, (3) GC-ox, (4) GC-ox/red. Electrolyte: dearated 0.25 M H_2SO_4 (pH 1); T = 25 °C; scan rate = 50 mV s^{-1}.