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Electrochemical evaluation of ferrocene carboxylic acids confined on surfactant–clay modified glassy carbon electrodes: oxidation of ascorbic acid and uric acid

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Abstract

We report on the electrochemical behavior of chemically modified glassy carbon (GC) electrodes by using surfactant/clay films, [cetyltrimethylammonium bromide (CTAB)/hydrotalcite-like], containing ferrocenecarboxylic (FC) or ferrocenedicarboxylic (FDC) acid. The results show that the surfactant molecules incorporated into the clay could increase the permeability and the positive surface of the film. The FDC–CTAB–clay–GC modified electrode showed greater stability and redox electroactivity than the FC–CTAB–clay–GC modified electrode. Low concentrations of ascorbic acid (H_2A) and uric acid (UA) in aqueous solution were easily oxidized on the FDC–surfactant–clay–GC modified electrode. The kinetic of the catalytic reactions were investigated by using cyclic voltammetry and rotating disk electrode. The results suggest that the oxidation of H_2A on FDC–CTAB–clay–GC electrode is limited by kinetics while the oxidation of UA is mass transport-limited. The FDC–CTAB–clay–GC modified electrode allows to determine H_2A in presence of UA, and shows good anti-fouling properties towards surface active materials.

Keywords: Ferrocene derivatives; Synthetic hydrotalcite-like clay; Ascorbic acid; Uric acid

1. Introduction

Electrodes modified by porous material films, such as clays, have been a very active research area [1–7]. The properties of the clays, such as, ionic interchange capacity, good catalytic support, great surface area, mechanical stability, low cost, etc. [8,9,10], make them suitable as electrode surface modifiers, despite its low electrical conductivity. A particular type of such material is the synthetic clay, whose structure is a hydrotalcite-like clay, $[M^{II}_{1-x}M^{III}_{x}(OH)_2][X^{n-}]_{x/n} \cdot yH_2O$ [7], which cast on surfaces as positive brucite-like layers, $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}$, intercalated by negative layers, $[(X^{n-})_{x/n}{\cdot}yH_2O]^{x-}$ [11,12]. They form stable thin films on glassy carbon electrodes; their composition provides a positively charged environment able to interchange ionized inorganic or organic molecules [13,14]. On the other hand, the interchange process may be enhance by cationic surfactants that increase the positive charge density of the film, providing a stronger interaction with the anion [15]. When the film is a composite of clay–surfactant, bilayers of the surfactant are believed to intercalate between clay layers [16].

The use of surfactants in electrochemical processes is well established in the literature [10,17]. Two of their properties are useful in electrochemistry, adsorption at interfaces and aggregation in supramolecular structures; those properties may improve the electrochemical behavior of the clay film.

The anionic ferrocene derivatives may be successfully interchanged on synthetic hydrotalcite-like clays [18]. Particularly, the ferrocenecarboxylic acid, have been used as mediators in a variety of electrochemical systems [17], mainly to facilitate enzymatic activity [19,20]. The basic unit of ferrocene (Fc), through a reversible oxidation process, generates the ferrocinium ion (Fc^+), under mild potential conditions.

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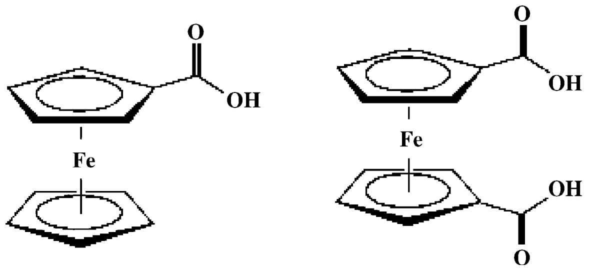

Scheme 1. (a) Ferrocenecarboxylic acid; (b) ferrocenedicarboxylic acid.

This characteristic makes ferrocene very convenient to be incorporated into supramolecular systems that need straightforwardly redox compounds at the electrode surface. The majority of ferrocene derivatives meet the conditions for ideal redox mediator: relatively low molecular mass, reversibility, regeneration at low potential, no pH dependent, generation of stable redox forms and they do not react with oxygen.

The present research report the electrochemical behavior of ferrocenecarboxylic and ferrocenedicarboxylic acid (Scheme 1) inside a surfactant/clay [cetyltrimethylammonium bromide/hydrotalcite-like clay] film on glassy carbon electrodes. We also study the catalytic activity on molecules of biological interest, such as ascorbic acid (H_2A) and uric acid (UA). Ascorbic acid is a vital component in human diet. It is known for its reductive properties, its antioxidant effect in foods and drinks, and its therapeutic use. Chemically modified electrodes, containing a variety of active mediators immobilized at the electrode surfaces, have been used in the oxidation of ascorbic acid in aqueous solution [21–25]. Although ascorbic acid is electroactive, it is too difficult to measure its direct oxidation on a conventional electrode, because of fouling of the oxidation products [26,27]. While the other compound considered, uric acid, is the primary end product of purine metabolism. It has been shown that extreme levels of UA in the body are symptoms of several diseases. Therefore, it is essential to develop simple and rapid methods for its determination in routine analysis. The results indicate that the modified electrode, especially when ferrocene dicarboxylic acid is used as the electroactive material, is stable, sensitive, and suitable to oxidize this type of organic compounds.

2. Experimental

2.1. Apparatus

Cyclic voltammograms were obtained by using a PAR potentiostat/galvanostat model 273A. The experiments were done in a gas-tight three-electrode cell containing a modified glassy carbon as working electrode (0.28 cm^2), a platinum-wire as counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The solution was purged and blanketed by nitrogen gas during the experiments.

The rotating disk electrode experiments were developed with a commercial rotating disk glassy carbon electrode Pine Instrument Co., and the pH measurements were done with a 26 pH meter. The thickness of the film was estimated from microphotographs using a scanning electron microscope HITACHI S-2500.

2.2. Reagents

Ferrocenecarboxylic acid (97%) and ferrocenedicarboxylic acid (96%) were purchased from Aldrich. Sodium chloride, sodium sulfate, sodium nitrate, and ascorbic acid (98.7%) were acquired from Merck. The surfactants, sodium dodecylbenzenesulfonic acid (SDBS), octylphenoxypolyethoxyethanol (Triton X-100) and cetyltrimethylammonium bromide (CTAB), were purchased from Riedel-de Haën. Uric acid was purchased from Cienvar and tetrabutylammonium perchlorate ($TBAClO_4$) was from Kodak. The nanohydrated aluminum nitrate (99%) and hexahydrated cobalt nitrate were purchased from Hopkin and Willian; sodium perchlorate, and sodium dihydrogen phosphate from Sigma. Water was purified by a Milli-Q reagent water system to specific resistance >15 MΩ cm. All other chemicals were reagent grade.

2.3. Preparation of the modified electrodes

The clay was synthesized in the laboratory following the coprecipitation method [28]. A solution containing 0.025 mmol of $Al(NO_3)_3$ and 0.075 mmol of $Co(NO_3)_2$ was titrated with 1 M solution of NaOH to produce a precipitate (clay). The layered structure of the clay was confirmed by powder X-ray diffraction (XRD). All solutions were purged with N_2 to avoid carbon dioxide and consequently obtain a clay, $[Co_{1-x}Al_x(OH)_2(NO_3)_x \cdot yH_2O]$, free from carbonate ions. The precipitate was filtered and dried for 24 h at 120 °C. A dispersion of 1 g of such clay in 50 mL of water and an aqueous dispersion of 1.2 mmol of CTAB and 2×10^{-2} mmol of FC or FDC in 20 mL were mixed and stirred at 30 °C for 1 h. The FC or FDC–surfactant–clay precipitate was filtered, washed and dried at 70 °C for 30 min. Then, a new dispersion, from the dried material, was prepared by sonication of 0.5 g of the precipitate in water. This dispersion was sonicated for 20 min immediately before preparing the films. The glassy carbon electrodes were previously polished, with alumina suspensions of different grain size (1.0 and 0.3 μm), on billiard cloth. After that, the electrodes were placed in a 1:1 methanol–water solution and properly cleaned in a sonicator for 5 min. FC or FDC–surfactant–clay films were prepared by casting 20 μL of the dispersion onto glassy carbon electrodes. Clay/surfactant films, free from electroactive species, were prepared by casting 20 μL of dispersion of 1 g of clay and 1.2 mmol of CTAB in 50 mL of water, sonicated for 20 min immediately before preparing films. These films were then dried in a closed container for 24 h. The thickness of the prepared films was approximately 3 μm,