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Ferrocenium strong adsorption on sulfonated polyaniline modified electrodes

Carlos Sanchís, Horacio J. Salavagione, Emilia Morallón *

Departamento de Química Física e Instituto Universitario de Materiales, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

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ABSTRACT

The electrocatalytic oxidation of ferrocene (Fc) at neutral pH in aqueous solution has been studied over thin films of electroactive sulfonated polyaniline (SPAN) by cyclic voltammetry. Strong adsorption of the oxidised species (ferrocenium ion) on the polymer arises as the explanation for the negative shift of the oxidation potential. FTIR-in situ studies provide further evidences of ferrocene/ferrocenium (Fc/Fc^+) adsorption and the sulfonate moieties in the polymer are proposed as adsorption sites. Adsorption of ferrocenium by cyclic potential sweep is suggested as a suitable method for its implementation into second generation biosensors based on SPAN polymer, where it would play the role of redox mediator.

1. Introduction

The study of the electrocatalytic abilities of conducting polymers is a common first-step approximation to asses their suitability to sensing applications. The electrocatalytic behaviour of polyaniline (PANI) towards a large list of redox species (metallic cationic complexes, halides, quinones) [1–3] in acidic aqueous media has been investigated during the last two decades. Exhaustive studies dealing with redox couples such as quinone/hydroquinone and Fe^{2+}/Fe^{3+} have been performed on electro-synthesized PANI [4–6] and a significant enhancement of reversibility of the redox heterogeneous reaction on the polymer film has been observed.

PANI self-doped derivatives which overcome common PANI main drawbacks, such as the restriction of its electroactivity to acidic media, are drawing increasing attention in order to confirm retention of PANI electrocatalytic properties in non-acidic media and finding new abilities provided by the modifying moieties. This is the reason why recently electrocatalytic studies have been extended to sulfonated polyanilines (SPAN) [7,8]. These sulfonated derivatives of PANI can be generated both by chemical or electrochemical copolymerization of aniline and aminobezenesulfonic acid, and also by post-modification of common PANI with sulphuric acid [9] or with nucleophilic anions [10,11]. Recently, it has been shown that a continuous modification of the properties of SPAN can be achieved by simply modifying the feed ratio of aniline to aminobenzenesulfonic monomers in the copolymerization method [12].

Ferrocene/ferrocenium (Fc/Fc^+) redox couple is well known because of its ability to yield fast electron transfer. It has been found that ferrocene yields highly reversible heterogeneous redox processes in most organic solvents, including ionic liquids. As a result, its heterogeneous electron transfer kinetics has been exhaustively studied and redox potential has been established in many different solvents [13–16], in order to use it as an internal potential reference in non-aqueous media. Ferrocene has also been thoroughly studied as an electron donor attached to the end of alkanethiols in SAMs generated over gold electrodes [17–19]. This constitutes a smooth, reproducible model that has provided a better understanding of the long-range electron transfer, which is a rather common phenomenon between redox proteins in biological systems. Nevertheless, Fc/Fc^+ electrochemistry has been rather low studied in aqueous solution since it shows no longer good reversibility. It has been reported that ferrocene weakly adsorbs over most common electrode materials with low influence of the electrolyte employed [20].

Because of its electron-transferring abilities, ferrocene has found application as “redox mediator” in amperometric biosensors, especially in those based on conducting polymer matrixes. Ferrocene behaves as an electron shuttle and it has been shown that it improves the electronic transfer between redox targets (i.e. active centres in enzymes) and the polymer matrix and/or the supporting electrode. It was introduced for the first time in an amperometric biosensor for the detection of glucose [21], after it had been claimed as an effective regenerator for the enzyme glucose oxidase [22], replacing molecular oxygen which is the natural cofactor.

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* Corresponding author. Tel.: +34 965909590; fax: +34 965903537.
E-mail address: morallon@ua.es (E. Morallón).

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Afterwards, biosensors based on conducting polymers have tried to incorporate this redox mediator either by physical entrapment [23,24] or by covalent binding to the polymeric structure [25,26]. However, both strategies for ferrocene inclusion in conducting polymer matrixes suffer of some drawbacks which have been outlined in a previous review of the topic [27].

In the present work, Fc/Fc$^+$ couple are intended to be used as a suitable redox target to study SPAN electrocatalytical abilities in neutral aqueous medium. This is a rather uncommon Fc/Fc$^+$ use, since its electrochemical behaviour in aqueous media still remains poorly understood, and usually species with a well-known (nearly reversible) behaviour are preferred to undertake fundamental studies. The background of this study is to assess the suitability of the Fc/Fc$^+$ couple as a redox mediator for SPAN based biosensors, operative at physiological conditions.

2. Experimental

2.1. Reagents

Aniline (Aldrich, p.a.) was distilled prior to use and stored at low temperature in the dark, 2-aminobenzenesulfonic acid (2ABSA) (Aldrich) and ammonium peroxodisulfate (Merck) and hydrochloric acid (Merck) of reagent grade were used without further purification. Di-potassium hydrogen phosphate (Merck, p.a.), sodium dihydrogen phosphate monohydrate (Merck, p.a.), ferrocenium hexafluorophosphate ($FcPF_6$) (Aldrich) and ferrocene (Aldrich) were also used as received. All solutions were prepared with purified water obtained from an Elga Labwater Purelab system (18.2 MΩ cm).

2.2. Chemical synthesis of sulfonated polyaniline

Sulfonated polyaniline (SPAN) was obtained as a copolymer using a common method of chemical oxidation with 0.1 M peroxodisulfate in an acidic medium (1 M HCl), with a feed ratio 80:20 (aniline to 2ABSA), setting a total monomer concentration of 0.1 M. The synthesis solution was kept under 5 °C during 1 h, then filtered and washed thoroughly with a cooled 1 M HCl solution and finally with water. The polymer was then dried under dynamic vacuum for at least 12 h. The actual sulfonation degree achieved was 11% according to the elemental analysis [12].

2.3. Electrochemical measurements

Modified electrodes of SPAN were obtained by casting a copolymer PANI-*co*-2ABSA aqueous solution in 1 M NH_4OH on the top of a bare glassy carbon (GC) electrode (LeCarbone Lorraine), 0.3 cm in diameter (0.071 cm^2), and then, the solvent is evaporated at room temperature. The flat surface of the GC was previously polished with 1 and 0.25 μm diamond suspensions over cloth and cleaned in ultra-pure water in an ultrasonic bath. The polymer solution was initially prepared by dispersing the copolymer in the alkaline solution to a final concentration of 1 mg/mL, being afterwards allowed to separate by decantation. In this way a low concentrated solution was obtained, since just a fraction of the copolymer was actually soluble. This soluble fraction corresponds with highly sulfonated, oligomeric chains of SPAN.

Solutions of SPAN employed had been long time stored in 1 M NH_4OH before they were used. This assures that all external doping has been removed from the polymer previously to its use in modified electrodes. Films of different thickness were prepared by depositing, respectively: (A) 10 μL and (B) 5 μL from the initial solution and (C) 5 μL from a four-fold dilution of the former, to obtain a relative ratio of thicknesses 8:4:1. The sample notation is A–C according to these amounts of solution casting on the GC electrode.

Solutions were prepared from a ferrocenium salt ($FcPF_6$) since it exhibits higher solubility in aqueous media than ferrocene (Fc) ($\approx 10^{-5}$ M) [17]. Fc$^+$ solutions were prepared 0.50, 0.25 and 0.125 mM in a 0.025 M phosphate buffered solution at pH 7.3. Due to low stability of Fc$^+$ in most solvents [28], solutions were stored in the dark at low temperature and were used only within 1–3 days after preparation.

Electrochemical measurements were performed in a classical three-electrode cell. A platinum wire was used as a counter electrode, a reversible hydrogen electrode (RHE) immersed in the same electrolyte was used as a reference electrode. All solutions were thoroughly deoxygenated with a flux of N_2 gas prior to the electrochemical tests. An initial characterization of the Fc$^+$ solutions was carried out by cyclic voltammetry (CV) at different scan rates using a platinum spherical electrode (0.148 cm^2) and a GC bare electrode (0.071 cm^2) as the working electrode.

2.4. In situ-FTIR spectroscopy

For the in situ-FTIR measurements a Nicolet Magna IR-spectrometer using a liquid nitrogen-cooled MCT detector was employed. The sample compartment was purged using a 75-50 Balston clean air package. The working electrode used was a platinum disc, 0.8 cm in diameter. The disc was mounted on a glass tube and it was polished using alumina powder of several sizes (1, 0.3 and 0.05 μm) to obtain a smooth reflecting surface. After the polishing the remainder alumina were removed by means of a cleaning process which consists on immersing the electrode in a diluted solution of KOH in an ultrasonic bath. After rinsing the platinum disc with abundant pure water, the SPAN film was deposited on its surface. Then voltammetric cycling at 50 mV s^{-1} was performed during 20 min between 0.0 and 1.0 V in a 0.50 mM $FcPF_6$ buffered solution, in order to introduce Fc$^+$ in the polymer and finally rinsed with phosphate buffer solution. SPAN-modified Pt electrodes with attached Fc$^+$ were immediately transferred into the spectroelectrochemical cell filled with phosphate buffer solution without dissolved Fc$^+$, and immersed at a fixed potential. The thin-layer spectroelectrochemical cell was provided with a prismatic CaF_2 window beveled at 60°. Spectra were collected at potentiostatic conditions with 8 cm^{-1} resolution.

Fourier transform infrared (FTIR) spectra in the transmission mode were obtained in KBr pellets of ferrocene and ferrocenium hexafluorophosphate in the same equipment at a 4 cm^{-1} resolution.

3. Results and discussion

3.1. Cyclic voltammetry study

The behaviour of the Fc/Fc$^+$ couple in aqueous buffered medium was studied by cyclic voltammetry on bare Pt and GC electrodes in 0.50 mM $FcPF_6$ solution. The voltammograms (Fig. 1) show a single redox process with the cathodic peak at 0.82 V corresponding to the reduction of Fc$^+$ and the anodic counterpart at 0.91 V due to Fc oxidation. The last one shows strong dependence in peak intensity with the electrode material.

For the GC electrode a high peak of Fc oxidation was observed with an anodic peak current density (jp_a) to cathodic peak current density (jp_c) ratio of 3. This behaviour is in accordance with that previously observed by Bond et al. [20], and can be explained as a result of *weak adsorption* of Fc on the electrode surface. Terms of weak and strong adsorption of reactant or product in a redox heterogeneous reaction were already used by Wopschall and Shain [29], who predicted typical shapes of cyclic voltammograms when