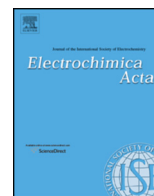




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Indirect amperometric detection of non-redox ions using a ferrocene-functionalized and oriented mesoporous silica thin film electrode

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ABSTRACT

Vertically oriented and ferrocene functionalized mesoporous silica thin films have been prepared by combining the electrochemically assisted self-assembly (EASA) method with click chemistry. The resulting films are electroactive, involving an electron hopping mechanism between adjacent ferrocene moieties. The electrochemical oxidation of ferrocene into ferricinium ion generates positive charges that are compensated by the ingress of anions into the film, opening the door to possible indirect amperometric detection of non-electroactive anions by flow injection analysis. Operating in an electrolyte-free flow, each injection of an anion (e.g., NO_3^-) at an electrode biased at a suitable positive potential (i.e., +0.5 V) gave rise to an amperometric response proportional to the anion concentration. However, to avoid the decrease of the electrochemical signal due to the progressive consumption of ferrocene in multiple successive analyses, it was necessary to regenerate the electrode by reduction of ferricinium moieties, which can be achieved in-situ by square wave amperometry. The feasibility to apply such indirect amperometric detection scheme in suppressed ion chromatography (for detecting anions in mixture) was also demonstrated.

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1. Introduction

The indirect amperometric detection of non-redox ions based on ion-to-electron transduction mechanisms constitutes an alternative to potentiometry at ion-selective electrodes [1–3]. This can be achieved using electrodes modified with electroactive conducting polymers [4–11] or inorganic thin films [12–14], for which the incorporation of ionic species is needed to counterbalance the electric charges generated by the electron transfer reactions. Examples are available for anions detection at oxidizable polymers such as polypyrrole [4–7], polyaniline [8] or poly(o-phenylenediamine) [9] modified electrodes, and for cations detection using reducible polypyrrole-dodecylsulfate [10], polydiphenylamine-dodecylsulfate [11], metal hexacyanoferrates [12,13] or mixed-valent ruthenium iron cyanide [14] composite films. Linear and reproducible responses can be obtained in the best cases [5], but sensitivity decrease upon successive analyses has been also reported [7], possibly due to selectivity changes in

relation with structural variations during the doping–undoping process [15]. Another approach relies on the use of electrodes modified with non-conductive ion-exchange materials (organic polymers [16] or inorganic zeolites [17–20]) filled with redox-active species. In this case, the electron transfer mechanism involves the exchange of the redox-active cations (or anions) by electrolyte cations (or anions) and the current response is directly related to the amount of exchanged mediators. In conditions of diffusion-controlled ion exchange processes, the recorded current signals can be proportional to the concentration of electroinactive ions in solution [16–20]. However, the progressive consumption of mediators from the material requires a chemical regeneration step between each measurement to avoid sensitivity decrease [18].

Electrodes modified with organic redox polymers constitute another category of electrochemical systems involving both electron transfer reactions and associated ion transport phenomena to maintain charge balance [21–23]. One can distinguish two kinds of such polymers depending on whether the redox moieties are immobilized either via weak or strong chemical bonds. The former family includes ion-exchange polymers incorporating redox ions that undergo charge transfer reactions according to two possible mechanisms, i.e., electron hopping between adjacent

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species or via molecular diffusion, or a combination of both, depending on the experimental conditions [24–28]. The second category consists in polymers to which the redox moieties have been covalently attached (resulting in intrinsically more durable immobilization), for which the electron transfer reactions involve electron hopping between redox centers with concomitant transport of electrolyte counterions for keeping electroneutrality [29–34]. Charge propagation is usually dominated by electron transport in such redox polymers [31–33], except at very low ionic strengths where ion transport might become the rate-determining step [33,34]. Note that their electrochemical response can suffer from variations in case of prolonged use due to structural changes (e.g., segmental between polymer chains [35], with mixed electron hopping and bounded diffusion during charge transport [36]). Such drawback can be circumvented to some extent by stiffening of the polymer structure (e.g., by cross-linking [37] or from designing block copolymer membranes with pendent redox moieties [38]), or by using mesoporous inorganic-organic hybrid materials which offer the advantage of a regular and rigid inorganic backbone ensuring good mechanical stability with the possibility to attach covalently electroactive functional groups on their internal mesopore walls [39–46].

In a previous work, we have prepared ferrocene functionalized mesoporous silica films with perpendicular pore channels and demonstrated that their electrochemical response, occurring via an electron hopping mechanism, was strongly influenced by the nature and concentration of the supporting electrolyte, as well as the ferrocene content in the material [45]. In the present work, we would like to exploit this behavior in which ferrocene oxidation into ferricinium cation requires the ingress of anions from the solution to maintain charge balance (see right part in Scheme 1), to investigate the indirect amperometric detection of electroinactive anions. The experiments will be performed by flow injection analysis using an electrolyte-free flowing stream, first by amperometry at constant potential and then in a square wave mode in order to regenerate the ferrocene moieties. The method will be also tested for the indirect amperometric detection of non-redox anions subsequent to chromatographic separation.

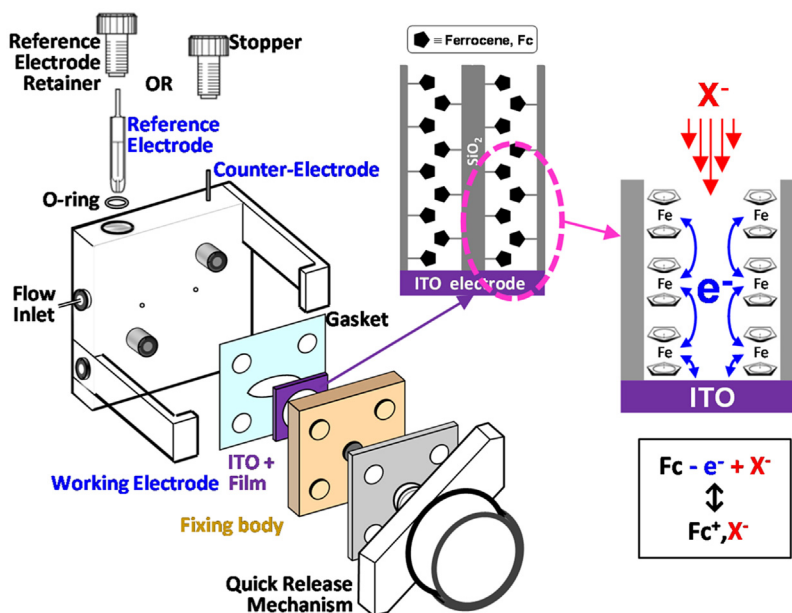
2. Experimental

2.1. Chemicals and reagents

3-chloropropyltriethoxysilane (Sigma Aldrich, 95%), sodium azide (Acros, 99%), tetrabutylammonium bromide (Sigma Aldrich, 99%) and acetonitrile (Sigma Aldrich, 99%) were used for the synthesis of 3-azidopropyltriethoxysilane (AzPTES) as previously described [46]. AzPTES, tetraethoxysilane (TEOS, Alfa Aesar, 98%), ethanol (Merck, 95–96%), NaNO_3 (Fluka, 99%), HCl (Riedel de Haën, 1 M solution), and cetyltrimethylammonium bromide (CTAB, Acros, 99%) were used for the film preparation. Hexaammineruthenium (III) chloride ($\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, Sigma-Aldrich, 98%) and ferrocenemethanol (Sigma-Aldrich, 97%) were used to check the quality of the azide-functionalized mesoporous silica thin films modified indium tin oxide (ITO) electrodes as previously described [43,45]. Ethynylferrocene, (Sigma Aldrich, 97%), ascorbic acid (Merck, 99%), copper acetate (Prolabo, 97%) and dimethylformamide (DMF, Sigma-Aldrich, 99%) were used for the preparation of the ferrocene-functionalized silica-based films from the azide-functionalized films via azide-alkyne cycloaddition reaction.

2.2. Preparation of the mesoporous films

The ferrocene-functionalized silica films have been prepared on ITO electrode by combining the electro-assisted self-assembly (EASA) [47,48] and co-condensation [49] methods driven to form vertically-aligned mesoporous films [50], with click chemistry [43,46]. Briefly, azide-functionalized mesoporous silica films were first generated from a solution containing the silica precursors (70 mM TEOS and 30 mM AzPTES) in the presence of the CTAB surfactant ($C_{\text{CTAB}}/C_{\text{silane}}$ ratio = 0.32) at pH 3 by addition of 0.1 M HCl. After hydrolysis of the silica precursors a cathodic potential was applied (-1.3 V for 20 s) in order to get the vertically oriented azide-functionalized films that were then aged for 12 h in an oven (120 °C). The surfactant template was removed by extraction in 0.1 M HCl ethanolic solution for 10 min. The azide-functionalized film electrodes were further functionalized by click coupling with



Scheme 1. Exploded view of the electrochemical flow cell (operating either with a reference electrode or using simply a stopper when working in a two-electrode configuration, with a schematic representation of the vertically-oriented, ferrocene-functionalized, mesoporous silica film on ITO electrode and, on the right a description of the electron transfer mechanism involving the ingress of the electrolyte anion (X^-) upon ferrocene oxidation into ferricinium ion.

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