Redox Induced Orientational Changes Occurring in a Ferrocene Derivative Monolayers Self-Assembled on Gold

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INTRODUCTION

The ease of preparation, close-packing and organisation of self-assembled monolayers (SAMs) on metals are some of the reasons that have encouraged a floury of research into this field over the last decade (1).
The adsorption of alkylthiols on gold is one of the most commonly examined systems in this field. The strong covalent bond established between sulphur and gold together with the interactions among the alkyl chains provide the stability required for the characterisation of these modified electrodes. The covalent attachment of a redox terminal group allows the use of several *in situ* structural techniques combined with electrochemistry (2).
The detection of any changes in coverage, thickness and orientation of the layers in contact with a solution under the application of an external potential can provide valuable information about the functional behaviour and stability of these layers for potential applications (3).
In the work presented here a set of short chained ferrocenylthiols [$(C_5H_5)Fe(C_5H_4)CO(CH_2)_nSH$] [n = 2, 3, 4, 5, 7 and 9; $(C_5H_5)Fe(C_5H_4)$ = Fc; FcC_n] which were successfully self-assembled on gold electrodes (4). The monolayers were characterised by cyclic voltammetry, *in situ* ellipsometry and *in situ* FTIR spectroscopy.

RESULTS AND DISCUSSION

The data showed that redox behaviour and structure of short chain monolayers is strongly dependent on the number of carbons. Interestingly, surface coverage of modified electrodes with odd numbered alkyl chain were lower than those with even alkyl chain. This suggests that chains are tilted and that most probably the area projected by the ferrocene moiety in the odd numbered chains is larger than in the even numbered chains.

In situ FTIR spectra of FcC_n modified electrodes were obtained at several potential values and normalised against the spectra acquired at 200 mV, where the ferrocene is in its reduced form. The differences in the IR spectra produced by ferrocene oxidation suggest that the redox process should be accompanied by a rotation of the ferrocene group where the plane of the cyclopentadienyl rings moves to a more perpendicular position in relation to the electrode surface. Analysis of the absorption bands of the methylene group indicates that little or no movement is associated to the alkyl chain during the ferrocene redox process.

The changes in the optical parameters, Ψ and Δ, were monitored during potential cycling and between two potential values (figure 1), where the ferrocene was either in its reduced or oxidised form. The optical changes point to an increase of 1-2 Å in the monolayer thickness as the ferrocene is oxidised to the ferricinium cation. The thickness variation is in good agreement with the FTIR data since the rotation of the ferrocene rings would cause a very small increase of thickness.

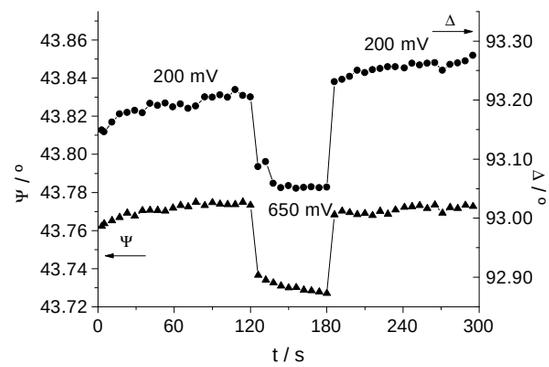

Figure 1 – Ellipsometric changes Δ (•) and ψ (▴), of a modified gold electrode with FcC_6 in 1.0 mol dm^{-3} $HClO_4$, at two different potentials: 200 and 650 mV.

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