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Cyclic Voltammetry Studies of Octadecanethiol Self-Assembled Monolayers in Different Concentrations of $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$

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Octadecanethiol self-assembled monolayers derivatized gold electrode in different concentrations of $Fe(CN)_6^{3-/4-}$ was studied by cyclic voltammetry. The cyclic voltammetric responses display a series of inverse sigmoidal curves for the SAMs in the solution of various concentration of $Fe(CN)_6^{3-/4-}$. A new concept of apparent effective thickness of self-assembled monolayers is established on the base of the measurements of cyclic voltammetry. It is determined that the apparent effective thickness of the SAMs is lower than the length of chain of octadecanethiol. Defect sites may be present in the alkanethiol monolayers. The apparent effective thickness can be used to describe the quality of SAMs quantitatively.

Keywords: Octadecanethiol; Cyclic Voltammetry; Self-assembled monolayers; Apparent effective thickness

INTRODUCTION

In the past decade, many works have been done by means of surface techniques and a great deal is already known about the SAMs organization and their insulating properties. If the SAMs are essentially free of pinholes, electron tunneling is the mechanism of electron transfer between redox solutes in solution and gold electrode [1]. But the highly ordered SAMs may have very small defects such as step edges, crystal grain boundaries in the underlying gold, tilt domain boundaries and other minor packing defects

within the monolayers. In the present paper, based on electrochemical measurements, we proposed a new concept, i.e. the apparent effective thickness to characterize the degree of thiol's order in the monolayers.

EXPERIMENTAL

Reagents and electrochemical methods were described previously [2]. SAMs was prepared according to the literature [3]. The octadecanethiol layer must be structurally well ordered and relatively pinhole-free. It should block the electrochemical reaction of dissolved ferricyanide species.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms of the SAMs/Au electrode in different concentrations of $Fe(CN)_6^{3-/4-}$. The cyclic voltamgrams do not show any microelectrode behaviors and the impedance–plane plots do not show any evidence of a low-frequency Warburg line [2]. As discussed by Porter et al.[3], this electron transfer process for $Fe(CN)_6^{3-/4-}$ at SAMs/Au electrode can be assigned to the electron tunneling process. The redox current at any potential should decrease exponentially with the monolayers thickness according to the Eq. (1)[1]

$$i = i_o \, e^{-\beta d} \tag{1}$$

$$i_o = n F k_s \exp\left(-\frac{\alpha n F}{RT}\eta\right) c \tag{2}$$

$$i = n F k_s \exp\left(-\frac{\alpha n F}{RT}\eta\right) e^{-\beta d} c = S c \tag{3}$$

$$S = n F e^{-\beta d} \, k_s \exp\left(-\frac{\alpha n F}{RT}\eta\right) \tag{4}$$

Where k_s is the standard electron transfer rate constant at bare Au electrode. The transfer coefficient α is assumed to be 0.5 and the k_s at bare Au

electrode is taken to be 0.026 $cm \cdot s^{-1}$ for $Fe(CN)_6^{3-/4-}$ [4], β is electron tunneling coefficient which is 1.02 / CH_2[1]. From Eq.(3), lines can be obtained from i vs c at a given overpotential (Fig.2).

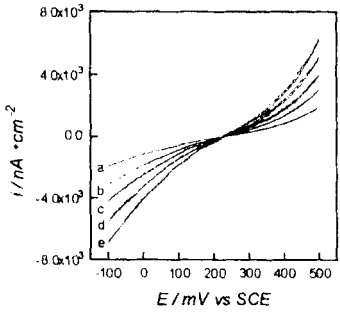

FIGURE 1 The cyclic voltammograms of modified gold electrode at 0.1 V / s in $Fe(CN)_6^{3-/4-}$ + 0.1 $mol \cdot L^{-1}$ KCl. The concentrations of $Fe(CN)_6^{3-/4-}$ are a 0.99; b 1.96; c 2.91; d 3.84; e 4.76 $mmol \cdot L^{-1}$ respectively.

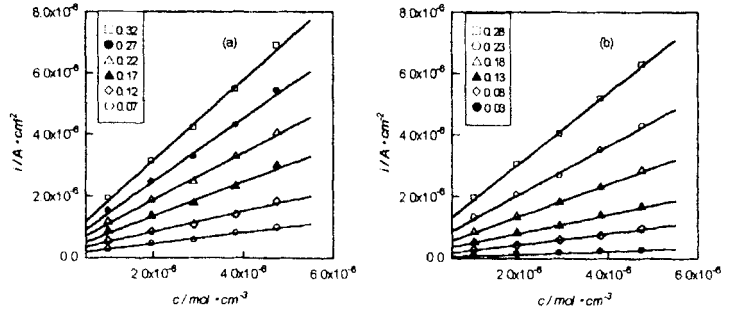

FIGURE 2 the plots of the current i vs c at different overpotentials as indicated in the figure, cathodic process (a), anodic process (b)

Fig.2 shows the plots of the current i vs the concentration at different overpotentials, the linear regress results are listed in Table 1. The apparent effective thickness, d can be obtained from the intercept of ln S ~ η

according to Eq.(4) (Table 1), which is far lower than the chain length of octadecanethiol. This result is consistent with that of determined by ac impedance spectroscopy in our laboratory.[5]

TABLE 1 Data from the measurements of cyclic voltammetry

	cathodic process	anodic process
η/V	0.07 0.12 0.17 0.22 0.27 0.32	0.03 0.08 0.13 0.18 0.23 0.28
S	0.18 0.33 0.55 0.76 1.02 1.31	0.05 0.18 0.30 0.52 0.79 1.15
I	-2.09	-2.42
R'	0.984	0.997
d / CH_2	9.7	10.1

* $\varphi^0 = 0.22$ V , $\eta = |\varphi - \varphi^0|$; S is the slope of i plots vs c. I is the intercept and R' is the correlation coefficient of ln (S) plots vs η, d is the apparent effective thickness of the SAMs in CH_2.

In conclusion, a new concept of the apparent effective thickness of the SAMs is proposed on the base of cyclic voltammetric measurement results. Though the cyclic voltamgrams do not show any microelectrode behavior, small defect sites may still be present in the SAMs. The apparent effective thickness can be used to describe the quality of SAMs quantitatively.

Acknowledgements

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