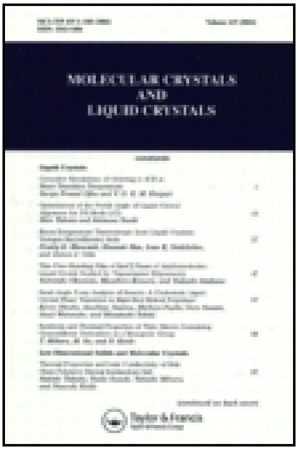

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Electrochemical Behavior of Self-assembled Monolayers(SAM) of ω-Mercaptoalkylhydroquinone on Gold

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Electrochemical Behavior of Self-assembled Monolayers(SAM) of ω-Mercaptoalkylhydroquinone on Gold

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The electrochemical properties of gold electrodes modified with ω-mercaptoalkylhydroquinone SAMs ($H_2Q(CH_2)_nSH$, n = 1, 4, 8, 12) were investigated by cyclic voltammetry. The electron transfer parameters and tunneling constant depending on the distance were evaluated.

Keywords: mercaptoalkylhydroquinone; self-assembled monolayer; cyclic voltammetry; electron transfer; tunneling constant.

INTRODUCTION

Self-assembled monolayers(SAMs)[1] on electrode surface are attractive as model systems for studies of interfacial electron transfer because they are stable and structurally well-defined interfacial monolayer with a controllable thickness and desirable function. This characteristics of SAMs affords an opportunity to study fundamental issues such as the effects of distance and interfacial structure on the long-range electron transfer kinetics between a redox active species and an electrode. The first direct information on electron-tunneling distance relationship was obtained for reduction of pentaamine-cobalt(III) complexes anchored to gold and mercury surface by Weaver and Li[2].

In this work, we report the determination of the electron tunneling constant and kinetic parameters for the long range electron transfer in the ω -mercaptoalkylhydroquinone SAMs on gold electrode.

EXPERIMENTAL

The electrochemical measurements were carried out in a single compartment cell with home-made Au electrode, platinum counter electrode, and saturated calomel electrode. Voltammetric experiments were performed with the use of a BAS 100B/W potentiostat. The electrolyte solutions were prepared with deionized water purified to a resistivity of 18 MΩ/cm and deaerated by purging with nitrogen. The Au bead electrode was cleaned by immersion for 10 min in a piranha solution prior to use. After rinsing with deionized water, ethanol and drying with nitrogen gas blowing, the gold electrode was immersed in 1 mM ethanol solution of $H_2Q(CH_2)_nSH$ for 2-5h.

RESULTS AND DISCUSSION

Figure 1 shows the typical cyclic voltammograms(CVs) for the spontaneously adsorbed $H_2Q(CH_2)_nSH$(n = 1, 4, 8, and 12) self-assembled monolayers on gold electrode, where the supporting electrolyte is aqueous 0.1 M $HClO_4$. These redox wave shapes are not changed to continuous potential cycling over 2 h period at room temperature, demonstrating that H_2Q-terminated monolayers are chemically and thermodynamically stable in acidic solution. In each voltammogram, a pair of redox peaks was observed due to the oxidation and reduction of hydroquinone which follows a two-electron and two-proton transfer reaction mechanism. The CVs in Figure 1(a-d) clearly demonstrate that the heterogeneous electron transfer kinetics of hydroquinone in SAM is dramatically transformed from reversibility to quasi-reversibility due to the longer spacer chain length in acidic condition. The faradaic charges estimated by the integration of redox peak area yield surface coverage values of (4.5 - 5.6) x 10^{-10} mole·cm^{-2}.

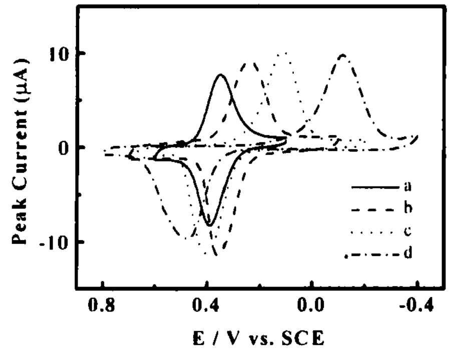

FIGURE 1. Cyclic voltammograms of $H_2Q(CH_2)_nSH$ self-assembled monolayers on gold (a-d for n= 1, 4, 8, and 12 in 0.1 M $HClO_4$. Scan rate was 100 mV · s^{-1}.

With a view to evaluating electron tunneling constant, we have investigated the electron transfer kinetics for hydroquinone redox centers in $H_2Q(CH_2)_nSH$ SAMs by cyclic voltammetry. According to Laviron's procedure[3], the standard rate constant and the electron

$$E_{pc}=E^{0'}_{c}-(RT/\alpha nF)\ln[\alpha nFv_c/RTk_{app}] \qquad (1)$$

$$E_{pa}=E^{0'}_{a}-(RT/(1-\alpha)nF)\ln[(1-\alpha)nFv_a/RTk_{app}] \qquad (2)$$

transfer coefficient(αn) can be determined from equation (1) and (2) by measuring variation of peak potentials(E_{pc}, E_{pa}) with scan rates(v_a, v_c) under totally irreversible condition. Using this procedure, the anodic and cathodic apparant rate constants(k_{app}) were obtained from the intercepts and slopes in the plots of E_p versus ln(v). Figure 2 shows the plot of the logarithmic heterogeneous apparent rate constant, the average value of the anodic and cathodic rate constant, as a function of the number of methylene groups of $H_2Q(CH_2)_nSH$ SAMs on gold. The slope in the plot shown in Figure 2 gives the β value of 0.92(± 0.11) per CH_2 unit using the number of methylene within alkyl chain spacer instead of absolute distance(Å) in our system. Currently, we are investigating the effects of pH, temperature, solution, surface coverage, spacer chain length, and coadsorption with diluent thiols on the heterogeneous electron transfer kinetics for hydroquinone-SAM system.

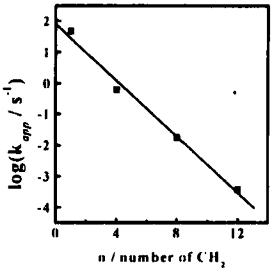

FIGURE 2. Distance dependence of log (k_{app} / s^{-1}) on the number of CH_2 group involved in the alkyl chain spacer of $H_2Q(CH_2)_nSH$(n= 1, 4, 8, and 12) SAMs on gold.

Acknowledgement

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