Electrochemical Characteristics of a 7-Ferrocenyl(carbonyloxy)-1-Heptanethiol-Modified Gold Electrode

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The electrochemical properties of 7-ferrocenyl(carbonyloxy)-1-heptanethiol [$FcCO_2(CH_2)_7SH$] were characterized by an electrochemical quartz crystal microbalance (EQCM). A gold surface was modified with $FcCO_2(CH_2)_7SH$ by the self-assembly method. EQCM was used to investigate mass change during the redox reactions of $FcCO_2(CH_2)_7SH$ monolayers on a modified gold electrode in solution containing $K_3Fe(CN)_6$ redox species. The $FcCO_2(CH_2)_7SH$ monolayer on gold acts as a mediator for the electron transfer between a gold electrode and electroactive species $Fe(CN)_6^{3-/4-}$ in solution. In both cases, electrochemical current responses were complicated because the observed currents were due to the redox of both the ferrocenyl group immobilized on gold and others in electrolyte solutions. The interfacial mass change (i.e. frequency change) on the gold electrode surface was observed during the redox of ferrocenyl groups.

Key Words: Electrochemical quartz crystal microbalance (EQCM), surface coverage, frequency, $FcCO_2(CH_2)_7SH$; $K_3Fe(CN)_6$

Introduction

Electroactive ferrocene is a prototypical redox group that has been frequently incorporated at the terminal site of alkanethiol-derivatized self-assembled monolayers (SAMs) on various electrodes[1,2]to study interfacial charge-transfer reactions dependent upon such variables as reaction driving force, distance, bridging groups, and the local microenvironment. However, these studies have mostly focused on $FcCO_2(CH_2)_7SH$ SAMs on polycrystalline Au surfaces. Investigations of the chemical modification of metal and semiconductor electrode surfaces by adsorption of functional molecules have been extensively carried out. The self-assembly method has been recognized as one of the most attractive approaches to create well-defined functional molecular layers on solid surfaces.[3] The most widely studied self-assembly system is the chemisorption of sulfur derivatives (i.e. thiols and disulfides) on gold.[4−10] Many scientists have reported the electrochemical characteristics of

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ferrocene alkanethiol SAMs on gold.[11−22] Ferrocene alkanethiol molecular layers on gold can be considered a model system for molecular electronic devices because the ferrocenyl group of the monolayer can exchange electrons readily with gold surfaces. It was found that the electrochemical responses of a gold electrode modified with a ferrocene alkanethiol monolayer were affected strongly by anions in solution because the ion-pairing between the ferricenium cation on the electrode surface and anions in solution occurred upon oxidation of the ferrocenyl group of the monolayers.[12,14,16,19,23−25] More direct evidence for the formation of ion-pairs was provided using an electrochemical quartz crystal microbalance (EQCM). Since the EQCM method has the capability of measuring mass change at the nanogram level at electrode surface/electrolyte interfaces,[16,19,21] it has been applied to understand various important phenomena, such as the transfer of ions and solvents during electrochemical redox changes,[16,19,21,26−31] detection of chemical and biochemical species,[32−37] deposition of metals on surfaces,[16,38−40] and the growth of molecular layers.[16,17,41−44] Uosaki et al. reported that the electron transfer between a gold electrode and redox species in electrolyte solution can be controlled using ferrocene alkanethiol monolayers. The well-packed monolayer of ferrocene alkanethiol on gold totally mediated electrons between gold and $Fe(CN)_6^{3-/4-}$ in solution.[45] The SAM of ferrocene alkanethiol transfers electrons for the reduction of Fe^{3+} and the oxidation of Fe^{2+} in solution.[17] However, these processes have been investigated only electrochemically; the detailed mechanisms involving the transport of counter ions have not yet become clear. In this paper, we investigated the surface coverage and mass change, i.e. interfacial mass transport at the $FcCO_2(CH_2)_7SH$-modified gold electrode surface during the redox reaction in solution containing other redox species using an EQCM system.

Experimental

Electrochemical measurements were conducted in a 3-electrode configuration. The electrochemical cell consisted of a quartz crystal gold electrode as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl (satd. KCl) electrode as the reference electrode. A commercial EQCM (Shin EQCN1000, Korea) was used for all electrochemical investigations. Potassium ferricyanide(III), perchloric acid, ferrocene carboxylic acid (97%), 1,6-dibromohexane (96%), CH_3CN, sodium sulfide, and THF were purchased from Aldrich, and used without further purification to prepare the electrochemical and electrolyte solutions with deionized water (resistivity: $> 18.2 \, M\Omega \, cm$). Gold evaporated on AT-cut 10 MHz quartz crystals was used in EQCM measurements. Mass sensitivity of the 10-MHz quartz crystals was 4.42 ng cm^{-2} Hz^{-1}. The EQCM measurements, using a frequency counter, were performed with a potentiostat. On cleaned AT-cut quartz crystal, Au and adlayer Ti were evaporated in high vacuum (ca. 1×10^{-7} torr) conditions with a Thermal and E-beam evaporation system (HVEB 200, Hanvac, Korea). The gold evaporated crystals were cleaned thoroughly with Piranha solution (a mixture of 98% H_2SO_4 and 30% H_2O_2 at 2:1 v/v). The average roughness factor and surface areas were calculated for the lab-made polycrystalline gold electrode as 1.2 and 0.26 cm^2, respectively. The cleaned gold polycrystalline substrate was modified by dip treatment in an ethanol solution containing $FcCO_2(CH_2)_7SH$ for 24 and 48 h. After the modification of the substrates, it was rinsed thoroughly with pure ethanol and then dried with a stream of N_2. Then the $FcCO_2(CH_2)_7SH$ monolayer-modified crystal was monitored with EQCM. The electrode current, potential and oscillating frequency of reference, and working electrodes were recorded simultaneously by EQCM. All the measurements were carried out at room temperature after the solution had been deaerated with dry

N_2 gas. The $FcCO_2(CH_2)_7SH$ was synthesized by our research group using ferrocenecarboxylic acid and 1,6-dibromohexane.

Results and Discussion

EQCM response of a gold electrode modified with $FcCO_2(CH_2)_7SH$ in $HClO_4$ solution

Figure 1 shows the cyclic voltammogram (CV) of the $FcCO_2(CH_2)_7SH$-modified gold electrode on a quartz crystal measured in 1.0 M $HClO_4$, with a sweep rate of 0.1 V s^{-1}. Reversible redox waves were observed around +0.52 V vs. Ag/AgCl. The waves observed on the positive-going potential scan and the negative-going potential scan are due to the oxidation and reduction, respectively, of the surface-attached ferrocenyl groups.[23] Mass change was calculated according to the Sauerbrey equation:

$$\Delta f = -2mn\Delta f_o^2/(\rho\mu)^{1/2} = -C_f m$$

where Δf is the frequency change caused by addition of a mass per unit area, m, to the crystal surface, n is the harmonic number of the oscillation (overtone number), μ is the shear modulus of the quartz (2.947×10^{11} g cm^{-1} s^{-2}), and ρ is the density of the quartz (2.648 g cm^{-3}). The constants are usually lumped together to yield a single constant, the sensitivity factor, C_f. The sensitivity of mass change of 10 AT-cut quartz crystal was 4.42 ng. Hz^{-1} cm^{-2}.

The charge in the cathodic peak is 0.314 μC cm^{-2}, which is equivalent to 1.6×10^{14} adsorbed molecules cm^{-2}, or surface coverage ($_{oxd}$) 2.71×10^{-10} mol cm^{-2}. The charge in the anodic peak is 0.334 μC cm^{-2}, which is equivalent to 1.73×10^{14} adsorbed molecules cm^{-2}, or surface coverage ($_{red}$) 2.88×10^{-10} mol cm^{-2}. This value is slightly smaller than the maximum coverage (4.48×10^{-10} mol cm^{-2}) calculated by assuming hexagonal close packing of the $FcC_{11}SH$[46].
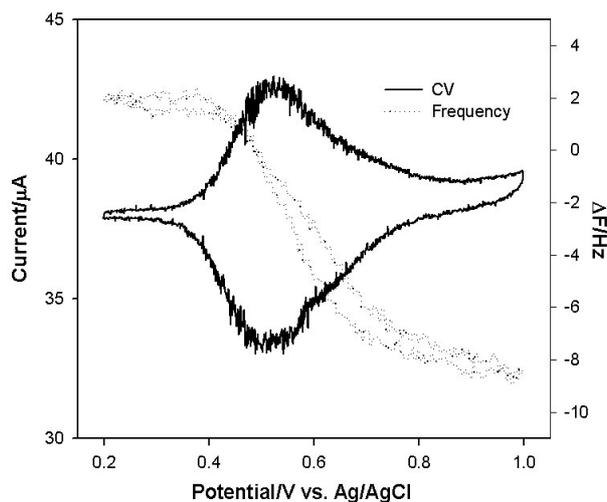
Figure 1. CV of a gold EQCM electrode dip-treated in 2 mM $FcCO_2(CH_2)_7SH$ ethanol solution for 24 h, measured in 1.0 M $HClO_4$ solution with a sweep rate of 0.1 V s^{-1}. Frequency change recorded simultaneously with potential cycling is included in this figure.

Figure 1 also shows the frequency change of the quartz crystal recorded simultaneously with the current during the potential cycling. The oscillation frequency decreased upon oxidation of the ferrocene moiety to the ferricenium cation, indicating the formation of an ion-pair between the ferricenium cation and perchlorate anion, as reported by Uosaki et al.[16,19,21,23] This process was reversible as the frequency returned to the initial value when the potential was more negative than the redox potential, so that the ferricenium cation was reduced to ferrocene. The total frequency change observed in this redox process was 11.5 Hz. From frequency change, mass transfer during redox reaction was calculated to be around 1.42×10^{-10} mol cm^{-2}.

The potential shifts were independent of the scan rates employed in this study (0.05 to 0.5 V s^{-1}) (Figure 2A). All the voltammograms at different scan rates showed well-defined surface waves consisting of symmetrical oxidation and reduction peaks at +0.57 V. These peaks are ascribed to the oxidation of the Fc moiety and the reduction of the Fc$^+$ moiety in the SAM film. Anodic and cathodic peak currents are shown at various scan rates (0.05 to 0.5 V s^{-1}) in Figure 2B. The current density increased linearly as the scan rate increased. This linear relationship indicates that electron transport in the $FcCO_2(CH_2)_7SH$ SAM film is fast enough at a scan rate of less than 0.5 V s^{-1} to oxidize or reduce all the Fc moieties in the film on Au surfaces. In Figure 2A, the typical CVs of the gold electrode modified with the SAM of $FcCO_2(CH_2)_7SH$ measured in 1.0 M HClO$_4$ at various scan rates (0.05 to 0.5 V s^{-1}) are seen. In all cases, symmetrical waves due to the redox of the Fc/Fc$^+$ couple were observed at $0.4 \sim 0.7$ V (vs. Ag/AgCl, satd. KCl), depending on ClO$_4^-$ anions.
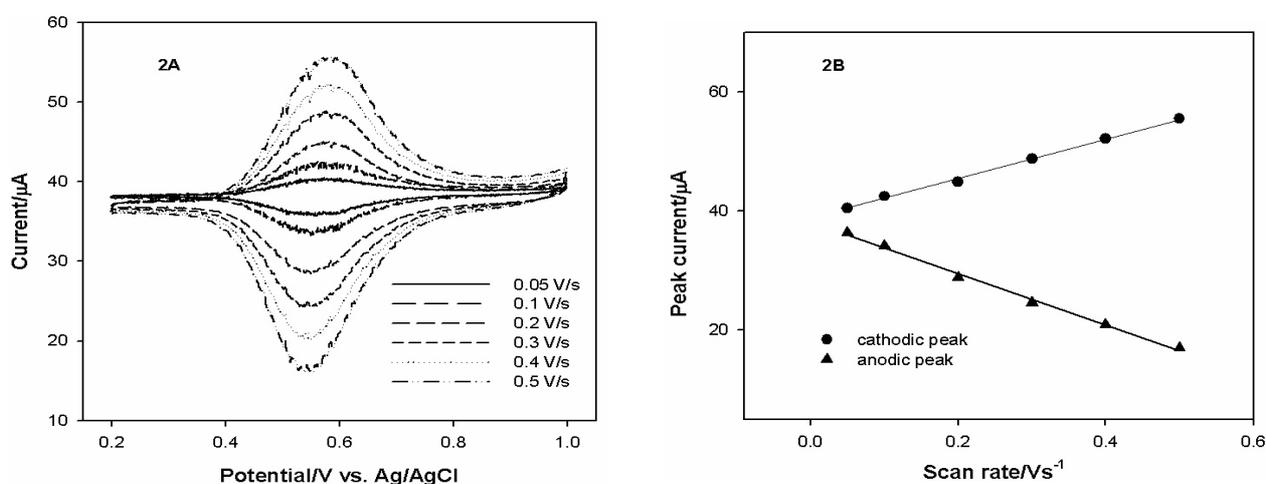
Figure 2. (A) CVs of gold modified with the SAM of $FcCO_2(CH_2)_7SH$ measured in 1.0 M HClO$_4$, with scan rates of 0.05 to 0.5 V s^{-1}. (B) Anodic and cathodic peak current of the $FcCO_2(CH_2)_7SH$-modified gold electrode in 1.0 M HClO$_4$ electrolyte.

EQCM response of $FcCO_2(CH_2)_7SH$-modified gold electrode in $K_3[Fe(CN)_6]$ + HClO$_4$ solution

Figure 3A shows CVs of the $FcCO_2(CH_2)_7SH$-modified gold electrode, which was used to obtain the result in Figure 1, and an unmodified gold electrode measured in 1.0 M HClO$_4$ solution containing 4 mM $K_3[Fe(CN)_6]$, with a sweep rate of 0.1 V s^{-1}. Reversible redox peaks were observed on the bare or unmodified

gold electrode around +0.56 V. In the case of the modified electrode, current peak waves were observed due to the redox of $Fe(CN)_6^{3-/4-}$ (+0.68 V: oxidation, +0.58 V: reduction) around +0.63 V and the Fc group (approximately +0.58 V) attached to the surface in Figure 3B. The redox behavior of $Fe(CN)_6^{3-/4-}$ on the modified electrode was completely reversible because the direct electron transfer between the $Fe(CN)_6^{3-/4-}$ and the gold electrode was mediated by the $FcCO_2(CH_2)_7SH$ monolayer.
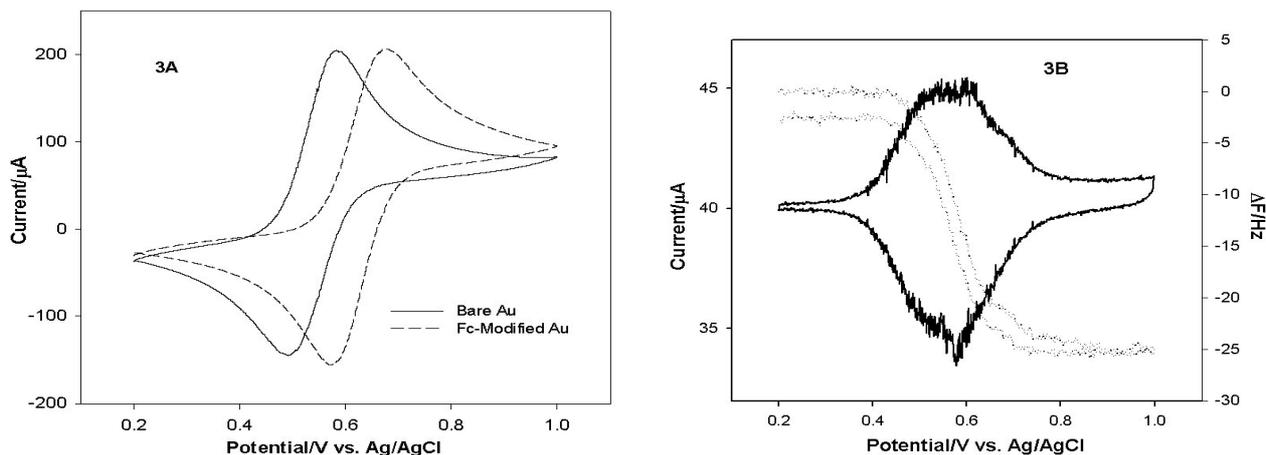
Figure 3. (A) CVs of 2 mM $K_3Fe(CN)_6$ using a bare gold electrode (solid line) and an $FcCO_2(CH_2)_7SH$-modified gold electrode (dotted line) in 0.1 M $HClO_4$ electrolytes, with a sweep rate of 0.1 V s^{-1}. (B) CV and frequency change at the $FcCO_2(CH_2)_7SH$-modified gold electrode (immersion for 48 h) recorded simultaneously with potential cycling.

The frequency change recorded simultaneously on the $FcCO_2(CH_2)_7SH$-modified gold electrode with potential cycling is shown in Figure 3B. The result of frequency change is very similar to that obtained without $Fe(CN)_6^{3-/4-}$ in solution (Figure 1). The frequency decreased upon oxidation of ferrocene and returned to its initial value on the reverse scans. The total frequency change was ca. 25.0 Hz. Mass transfer from frequency change was calculated as 3.08×10^{-10} mol cm^{-2}. Frequency change occurred around +0.58 V potential, showing that the frequency change is due to the redox reaction of the ferrocene moiety. Mass change was about 2.88×10^{-10} mol cm^{-2}, as seen in Figure 3B. The surface coverage of the anodic and cathodic peaks were $\Gamma_{red} = 3.51 \times 10^{-10}$ mol cm^{-2} and $\Gamma_{oxd} = 3.25 \times 10^{-10}$ mol cm^{-2}, respectively.

Conclusion

We carried out an EQCM study of a gold electrode modified with an $FcCO_2(CH_2)_7SH$ monolayer in solution containing other redox species $K_3Fe(CN)_6$ to monitor the mass change during the potential cycling. It was found that the mass change occurred by the adsorption and desorption of ClO_4^- anions on the electrode surface as a result of oxidation and reduction, respectively, of the Fc group. Although the voltammograms observed in the solution containing $Fe(CN)_6^{3-}$ were complicated, it was possible to separate the current component due to the redox reaction of Fc groups from that of others by the comparison of the measured voltammograms.

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