

Faradaic impedance titration and control of electron transfer of 1-(12-mercaptododecyl)imidazole monolayer on a gold electrode

Seongpil Hwang^{b,1}, Bang Sook Lee^{a,1}, Young Shik Chi^b, Juhyoun Kwak^{b,*},
Insung S. Choi^{b,**}, Sang-gi Lee^{a,**}

^a Division of Nano Science (BK21), Ewha Womans University, 11-1 Daehyun-Dong, Seodaemun-Gu, Seoul 120-750, Republic of Korea

^b Department of Chemistry and School of Molecular Science (BK21), KAIST, Daejeon 305-701, Republic of Korea

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Abstract

In this work, we studied interfacial proton transfer of the self-assembled monolayer (SAM) of 1-(12-mercaptododecyl)imidazole on a gold electrode by faradaic impedance titration method with $\text{Fe}(\text{CN})_6^{3-}$ as an anionic redox probe molecule. The surface $\text{p}K_{1/2}$ was found to be 7.3, which was nearly the same as that of 1-alkylimidazole in solution. We also investigated the electrochemical properties of the SAM-modified electrode by cyclic voltammetry. Cyclic voltammetry was performed (1) in the solution containing $\text{Fe}(\text{CN})_6^{3-}$ with repeated alternation of pH values to investigate the electrostatic interaction of the protonated or deprotonated imidazole with $\text{Fe}(\text{CN})_6^{3-}$ and (2) in the acidic or basic electrolyte containing $\text{Ru}(\text{NH}_3)_6^{3+}$ as a cationic redox probe to verify the effect of the polarity of a redox probe. We observed the reversible adsorption/desorption of $\text{Fe}(\text{CN})_6^{3-}$ and concluded that the adsorbed $\text{Fe}(\text{CN})_6^{3-}$ catalyzed the electron transfer of both $\text{Fe}(\text{CN})_6^{3-}$ itself and cationic $\text{Ru}(\text{NH}_3)_6^{3+}$.

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1. Introduction

The electrostatic interactions associated with charges of acid/base groups in proteins play a significant role in protein functions [1,2]. Particularly, histidine bearing an imidazole ring is the most frequently involved amino acid in the functional portion of proteins largely due to the chemical versatility of imidazole moiety, such as protonated form, deprotonated form, and tautomeric states [3,4]. Though the $\text{p}K_a$ value of imidazole of histidine is known to be 6.0 in solution [5], each imidazole of histidine in proteins has evolved for the optimum $\text{p}K_a$ for their function by varying microenvironment indicating the great effect of the protonation/deprotonation. Apart from the biological systems, the electrostatic interactions in chemically modified, artificial interfaces, such as self-assembled mono-

layers (SAMs) of alkanethiols on gold, are also important in the design of highly selective interfaces for sensors and functional interfaces. To control the selectivity, one must understand the interaction between interface and analyte in solution. The electron transfer through SAMs can provide us the detailed information about both the SAMs themselves and interactions between the substrate and ions in solution. Several researchers have reported electrochemical studies on electrostatic interaction between charged SAMs and charged redox molecules in solution [6–10]. They all, however, use the SAMs terminating in carboxylic or amine groups. Although these two functional groups have many advantages including commercial availability and the formation of well-ordered SAMs on gold, information on the electrostatic interactions of other functional acid/base groups, especially imidazole, is still required to design artificial interfaces for highly selective sensors and nanoelectronics, as well as to understand the biological functions of histidine at surfaces or active sites of proteins.

Recently, we reported the unique physicochemical properties of SAMs containing imidazole derivatives. The SAM of 1-(12-mercaptododecyl)-3-methylimidazolium bromide was

* Corresponding author. Tel.: +82 42 869 2833; fax: +82 42 869 2810.

** Corresponding authors.

E-mail address: Juhyoun_Kwak@kaist.ac.kr (J. Kwak).

¹ These authors contributed equally to this work..

found to show anion-directed, switchable properties including the wetting property (hydrophobicity/hydrophilicity) [11,12] and the electron transfer [13]. We also achieved the pH-dependent current rectification by using the SAM of 1-(12-mercaptododecyl)imidazole based on the asymmetric electrostatic interactions [14]. Although these results demonstrated unprecedented properties of imidazolium and imidazole moieties on SAMs, the intrinsic basic properties of imidazole on SAMs, such as surface $pK_{1/2}$ and electron transfer, have not been studied yet. In this work, we studied the electrochemical properties of the SAM of 1-(12-mercaptododecyl)imidazole to determine the surface $pK_{1/2}$ (pH value when a half of the imidazole is ionized) and the electron transfer kinetics involving the electrostatic interactions between the imidazole of the SAM and charged redox-active molecules in solution. As illustrated in Scheme 1, the deprotonated imidazole is formed in alkaline solutions (above the surface $pK_{1/2}$), and therefore negatively charged $\text{Fe}(\text{CN})_6^{3-}$ does not interact with imidazole electrostatically. In contrast, when most of imidazoles are positively charged due to the protonation in acidic solutions, cationic imidazoles would attract strongly $\text{Fe}(\text{CN})_6^{3-}$. Hence, due to the gradual deprotonation of surface imidazoles, the increase of solution pH would decrease the attractive force between imidazole and $\text{Fe}(\text{CN})_6^{3-}$. To investigate the effects of pH on the electron transfer of the negatively charged $\text{Fe}(\text{CN})_6^{3-}$ through the SAM of 1-(12-mercaptododecyl)imidazole, cyclic voltammograms (CVs) were recorded at various pH values. $\text{Fe}(\text{CN})_6^{3-}$ has been used frequently as a negatively charged probe to test the effect of pH, because both peak current and peak potential are steady in the wide pH ranges [10,15,16]. To determine $pK_{1/2}$, electrochemical impedance spectroscopy (EIS) was performed on the SAM of 1-(12-mercaptododecyl)imidazole in the electrolytes of various pH values. The more acidic, the smaller is the charge-transfer resistance due to the electrostatic attraction between the protonated imidazole and anionic $\text{Fe}(\text{CN})_6^{3-}$. The surface $pK_{1/2}$ of the SAM was determined by plotting the titration curve of pH and charge-transfer resistance. To investigate

the electrostatic interaction, three independent experiments were performed under different conditions: (1) the switching of the electron transfer by variation in pH was observed in the solution containing $\text{Fe}(\text{CN})_6^{3-}$ as an anionic redox-active probe, (2) ruthenium hexamine ($\text{Ru}(\text{NH}_3)_6^{3+}$) was used as a cationic redox-active probe both in acidic and basic conditions, and (3) the electrochemical property of the SAM-modified electrode pre-soaked in the solution containing $\text{Fe}(\text{CN})_6^{3-}$ was investigated in the solution containing $\text{Ru}(\text{NH}_3)_6^{3+}$. Experiments of (1) and (2) provides the electrostatic interactions between immobilized imidazole and charged molecules in solution while experiment (3) shows the effect of the adsorption of redox-active molecule on the electron transfer.

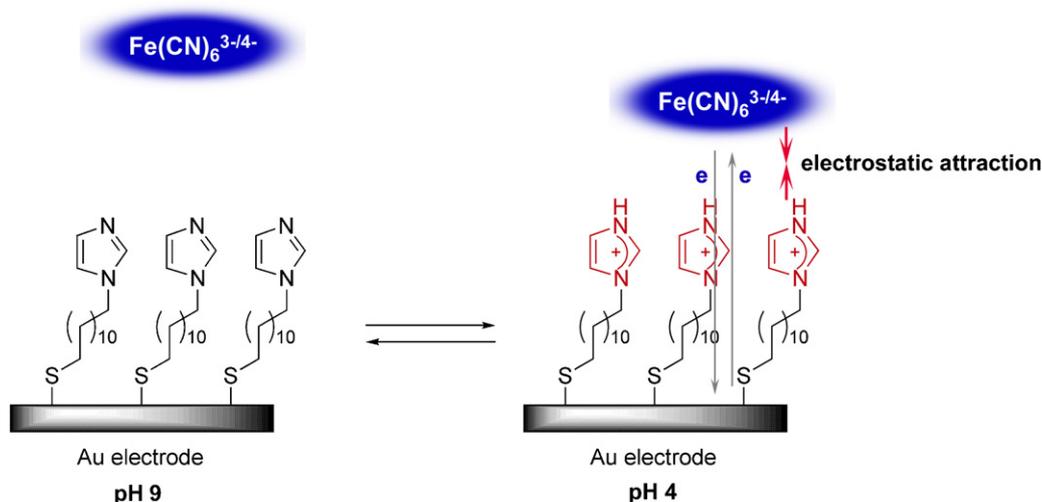
2. Experimental

2.1. Chemicals

$\text{K}_3[\text{Fe}(\text{CN})_6]$ (Mallinckrodt chemicals), $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ (Aldrich) and all other chemicals (obtained from Aldrich or Sigma) were analytical or better grades, and used as received. 1-(12-Mercaptododecyl)imidazole was synthesized as described in our previous report [14]. Ultra-pure water ($>18\text{ M}\Omega$) from a Modulab water system (US Filter Corp.) was used throughout this work. All glassware and electrochemical cell was cleaned in Nochromix (Godax Lab., Inc.) cleaning solution and then rinsed with ultra-pure water.

2.2. Preparation of self-assembled monolayers

The gold substrates were prepared by thermal evaporation of 5 nm of titanium and 100 nm of gold onto silicon wafers. Prior to use, gold substrates were cleaned for 1 min in piranha solution (3:7 by volume of 30% H_2O_2 and H_2SO_4 , *Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care*), rinsed with H_2O and ethanol, and dried under a stream of argon. The SAMs of 1-



Scheme 1. A schematic illustration of electrostatic interactions between ferricyanide and imidazole. While the deprotonated imidazole does not interact with ferricyanide at pH 9, the protonated imidazole at pH 4 attracts ferricyanide electrostatically.

(12-mercaptododecyl)imidazole were prepared by immersing the gold substrates in a 1 mM ethanolic solution of 1-(12-mercaptododecyl)imidazole overnight. After the formation of SAMs, the substrates were rinsed with ethanol several times and then dried under a stream of argon.

2.3. Electrochemical measurements

Electrochemical experiments were performed using an Autolab potentiostat PGSTAT 10 (Ecochemie, Netherlands). The three-electrode electrochemical cell consisted of the modified Au electrode, a Pt wire counter electrode, and a Hg/Hg₂SO₄ (mercury sulfate electrode: MSE, saturated K₂SO₄) reference electrode. The electroactive area of the electrode is 0.283 cm². Cyclic voltammetry and electrochemical impedance were measured in this electrochemical cell.

The electrochemical cell was filled with the pH-adjusted electrolyte solution of 0.1 mM K₃Fe(CN)₆ or Ru(NH₃)₆³⁺. A buffered electrolyte solution having a constant ionic strength was prepared using the method of Smalley et al. [17]. An aqueous solution of H₃PO₄ (0.01 M) having *ca.* pH 2.1 was used as an initial solution. The higher pH was adjusted by the addition of 0.11 M NaOH by measuring with a calibrated pH meter (3202BN probe and model 310, ThermoOrion, USA).

Cyclic voltammetry was performed with the pH-adjusted electrolyte solution using general purpose electrochemical systems (GPES data processing software, Eco Chemie). Afterwards, the impedance monitoring was done with the formal potential of the redox probe, by the application of a multiple sine waves using frequency response analyzer (FRA, Eco Chemie). In this mode, five frequencies are applied together, with amplitude of 5 mV (RMS) for each frequency. Each set of five frequencies consists of 30 discrete base frequencies from 50 mHz to 2 kHz, automatically combined with four additional frequencies calculated by the base frequency 3×, 5×, 7× and 9×. The data are represented in the complex plane ($-Z''$ vs. Z' , Z'' is the imaginary impedance and Z' is the real impedance). The impedance spectra are fitted to a modified Randles equivalent electrical circuit for the SAM-modified electrode, including the solution resistance (R_s), a constant phase element (CPE), the charge-transfer resistance (R_{ct}), and Warburg impedance (Z_w). The respective semicircle diameter correspond to the interfacial charge-transfer resistance (R_{ct}) of which values are calculated from the nonlinear least-squares (NLLS) fitting program of FRA. R_s is the resistance of electrolyte which the current must pass through. Instead of an ideal capacitor to account for nonfaradaic charging of the double layer, the CPE is used to compromise errors due to microscopic roughness and atomic scale inhomogeneity in the surfaces [18]. R_{ct} provides us with an indication of the kinetics of charge transfer at the SAM-modified gold. Z_w represents the hindrances of mass transfer. Fitting constraints were imposed such that further iterations were stopped when the chi-square (χ^2) change was less than 0.001% compared to the previous iteration. The goodness of fit was assessed from minimum χ^2 , correlation matrix and relative error distribution plots, less than 5% fluctuations between the experimental and fitted data were assumed

to be satisfactory in confirming the validity of the equivalent circuit.

3. Results and discussion

3.1. Effect of electrostatic interactions on electron transfer of anionic redox-active probe, Fe(CN)₆³⁻

Fig. 1 shows a great effect of the electrostatic interactions on the rate of the electron transfer. In the acidic solution (pH 4), reversible voltammetric behavior was observed. In this low pH, the peak current is proportional to the square root of the scan rate demonstrating the diffusion-controlled process. However, the charge transfer can be suppressed upon pH increase. The peak current is decreased and the difference between anodic and cathodic peak potentials (ΔE_p) increased. Finally, the electron transfer was nearly blocked at pH 9. In the absence of the SAM, pH-independent current is observed on the bare gold electrode [9]. These results clearly suggested that at lower pH values, the cationic, protonated imidazole attracts Fe(CN)₆³⁻ electrostatically and/or induced a partial adsorption of Fe(CN)₆³⁻ onto the SAM surfaces. In contrast, the fully deprotonated imidazole at higher pH values does not attract Fe(CN)₆³⁻ and the SAM of 1-(12-dodecyl)imidazole hindered the electron transfer, because SAMs containing long-alkyl chains blocked the electron transfer through electron tunneling, permeation, and diffusion.

In order to investigate the reversibility of protonation/deprotonation of the imidazole moiety of the SAM and its effect on the electron transfer of Fe(CN)₆³⁻, the pH of the electrolyte was altered by exchanging the electrolyte. In the acidic solution containing Fe(CN)₆³⁻, voltammetric behavior indicated quasi-reversible kinetics of electron transfer (solid line in Fig. 2a). In contrast, suppressed electron transfer in the basic solution was observed (dashed line in Fig. 2a). By repeated pH alternation of the electrolyte between the values 4 and 9, the electrochemical response of Fe(CN)₆³⁻ could be activated or deactivated reversibly (Fig. 2b). In addition to the electrostatic attractions, the surface-confined Fe(CN)₆³⁻ seemed to enhance the electron

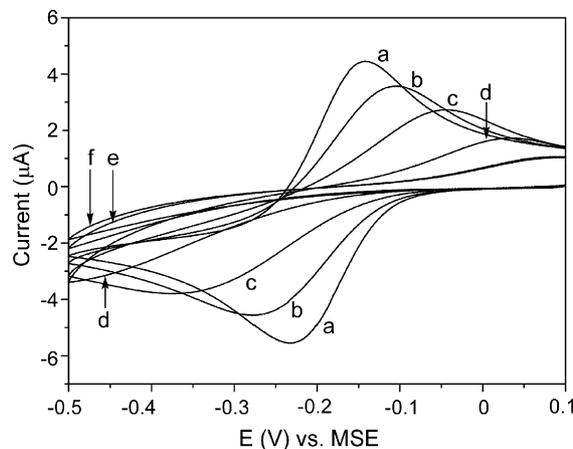


Fig. 1. CVs for the redox reactions of 0.1 mM Fe(CN)₆³⁻ at a pH of (a) 4, (b) 5, (c) 6, (d) 7, (e) 8, and (f) 9 solutions of 0.1 M ionic strength on the SAM of 1-(12-mercaptododecyl)imidazole. Scan rate is 50 mV/s.

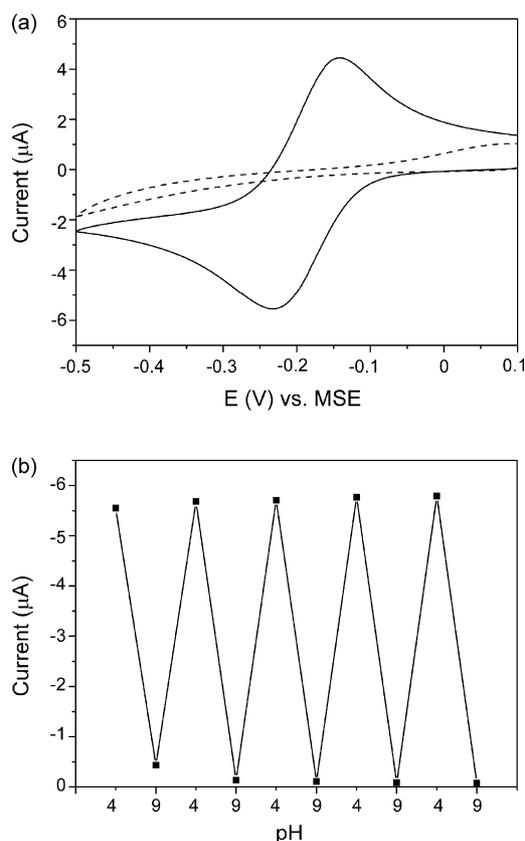


Fig. 2. (a) CVs of 0.1 mM $\text{Fe}(\text{CN})_6^{3-}$ solution at the SAM-modified gold at pH 4 (solid line) and pH 9 (dashed line). (b) Variation of the cathodic peak current during the repeated alternation of pH.

transfer *via* electron transfer self-exchange (ET self-exchange) [9]. After soaking the SAM-modified electrode in the acidic solution containing $\text{Fe}(\text{CN})_6^{3-}$, the adsorption of $\text{Fe}(\text{CN})_6^{3-}$ onto the SAM was confirmed by XPS (Fig. 3). Similar to previous reports [9,13], the adsorbed $\text{Fe}(\text{CN})_6^{3-}$ functioned as sites of electrocatalysis for electron transfer between the electrode and electroactive ions in solution, leading to the activation of the electrochemical response. In addition, the XPS study con-

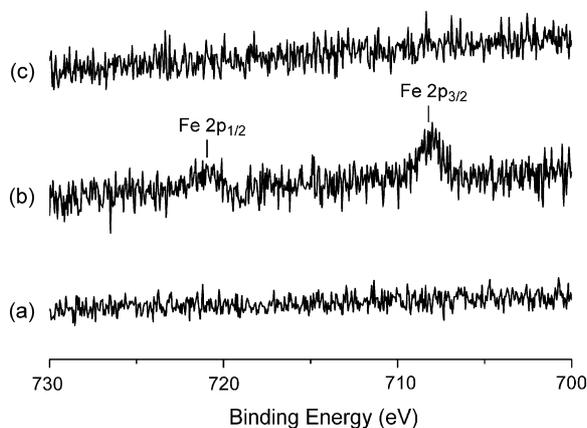


Fig. 3. Narrow-scan XPS spectra of the Fe 2p region acquired from the SAM of 1-(12-mercaptododecyl)imidazole (a) before and (b) after soaking in the acidic $\text{Fe}(\text{CN})_6^{3-}$ solution, and (c) after soaking the gold substrate presenting adsorbed $\text{Fe}(\text{CN})_6^{3-}$ in the basic solution.

firmed that the adsorbed $\text{Fe}(\text{CN})_6^{3-}$ was desorbed completely in the basic solution due to the deprotonation of imidazole (Fig. 3c). Based on these observations, we concluded that the protonation/deprotonation of imidazole and the concomitant adsorption/desorption of $\text{Fe}(\text{CN})_6^{3-}$ were reversible processes, and the electron transfer of $\text{Fe}(\text{CN})_6^{3-}$ was enhanced under the acidic condition.

3.2. Determination of surface $pK_{1/2}$ of 1-(12-mercaptododecyl)imidazole on gold using faradaic impedance titration

The electrostatic interactions between the imidazole and $\text{Fe}(\text{CN})_6^{3-}$, indicator for degree of protonation, could be measured quantitatively by electrochemical impedance spectroscopic studies of the charge-transfer resistance. We performed impedance titration using $\text{Fe}(\text{CN})_6^{3-}$ as a redox probe to determine the surface $pK_{1/2}$ of the SAM of 1-(12-mercaptododecyl)imidazole. Fig. 4 shows impedance complex plane plots recorded at various pH values. Changes in these impedance complex plane plots at different pH values confirmed that the deprotonation of imidazole obstructed the charge flow through the SAM. The simple model of modified Randle circuits, shown in Scheme 2, was used to derive the charge-transfer resistance. The titration curves of the impedance were plotted as a function of solution pH (Fig. 5a). The surface $pK_{1/2}$ was defined as the pH value when a half of the imidazoles were ionized, and estimated from the midpoint of inflection of the titration curves, assuming that a half of the bases were deprotonated at that point. Based on the plot, the surface $pK_{1/2}$ value was determined

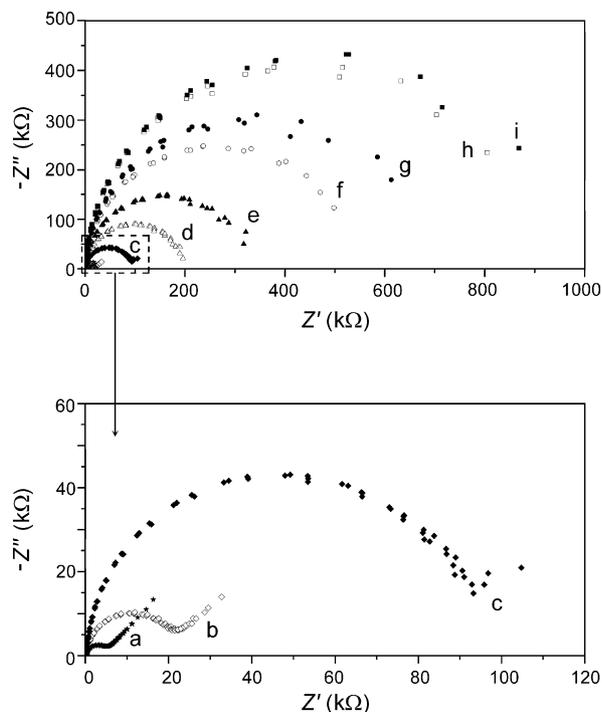
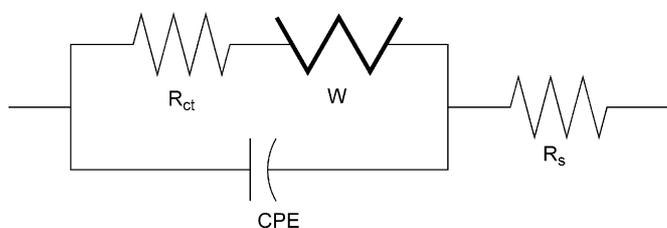


Fig. 4. Impedance complex plots of the impedance of the SAM-modified gold in the presence of 0.1 mM $\text{Fe}(\text{CN})_6^{3-}$ at a pH of (a) 4, (b) 5, (c) 6, (d) 6.5, (e) 7, (f) 7.5, (g) 8, (h) 8.5, and (i) 9 solutions of 0.1 M ionic strength.



Scheme 2. The modified Randles circuit model for a modified gold electrode. R_{ct} and R_s are interfacial charge-transfer resistance and uncompensated solution resistance, respectively. CPE is constant phase element associated with the charge double layer at the modified electrode. W is the Warburg element.

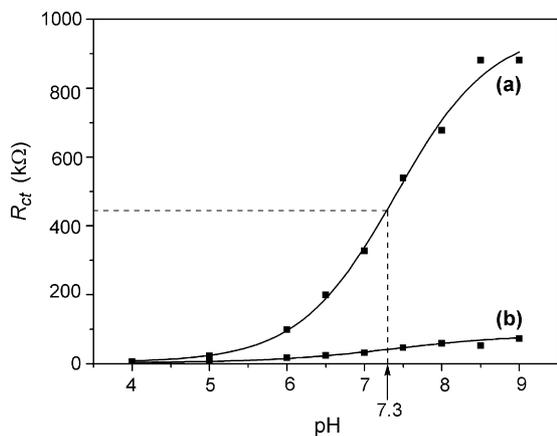


Fig. 5. Faradaic impedance titration curves for (a) the intact SAM of 1-(12-mercaptododecyl)imidazole and (b) the SAM of 1-(12-mercaptododecyl)imidazole which experienced repeated potential sweep in the acidic electrolyte containing ferrocenemethanol.

to be 7.3. The pK_a of 1-ethylimidazole, a structurally similar compound, is 7.3 in solution [19]. Generally, $pK_{1/2}$ values of acid/base groups in the SAM are shifted toward the neutral pH, because the charge–charge repulsion between closely located acid/base groups builds up as the extent of ionization increases [16]. In contrast to these general phenomena, $pK_{1/2}$ of imidazole in the SAM was nearly the same as that in the solution, indicating very small in-plane interactions among imidazole groups. The titration curve observed experimentally would be broader than that in the solution due to the electrostatic interactions at the monolayer/solution interface [20]. It should be noted that faradaic impedance titration was useful to determine the $pK_{1/2}$ of the terminal imidazole of the SAM owing to the well-defined results, while contact angle titration was not suitable because of the ill-defined contact angles [21].

In our previous study using the SAM of 1-(12-mercaptododecyl)imidazole, we found an intriguing phenomenon during the CV experiments using ferrocenemethanol as a redox probe [14]. Briefly, when a potential scan was applied to the SAM-modified electrode in the acidic solution containing 0.5 mM ferrocenemethanol (pH 2), the gradual increase in the oxidation current was observed, indicating the structural change of the SAM, and the electrode became more accessible to ferrocenemethanol. This phenomenon was not found when $Fe(CN)_6^{3-}$ was used as a probe or the experiment was conducted in the basic solution. After these potential scans

involving the structural change, unprecedented rectifying current was observed on the SAM-modified electrode, which was probably due to the asymmetric electrostatic interactions [14], the conformational change [22], and/or the localized electronic effect [23]. To investigate the effect of this structural variation on the charge-transfer resistance of the SAM-modified electrode and on the surface $pK_{1/2}$, we performed faradaic impedance titration on the electrode that had experienced the potential sweep in an acidic solution containing ferrocenemethanol (Fig. 5b). While the $pK_{1/2}$ was not changed after the potential sweep, the value of the charge-transfer resistance decreased by *ca.* 93% (only 7% of resistance remained), compared with that of the original SAM-modified electrode. The reduced charge-transfer resistance indicates that $Fe(CN)_6^{3-}$ communicated with the SAM-modified electrode more easily after the structural change. One of possible reasons for this phenomenon is the opening of channels (or more defects) in the SAM through the partial desorption or the formation of 2D aggregated domains of thiol molecules [24]. However, there were no significant change in the charge of thiol-reductive desorption (Fig. 6a) and of Cu underpotential deposition (Fig. 6b) indicating the conservation of the quantity of adsorbed thiols and no channel allowing diffusion of Cu^{2+} . Thus, increased channel (or more defects) in the SAM is hardly expected. To explain the conservation of the $pK_{1/2}$ value and the decreased charge-transfer resistance, we propose the disorder of the SAM by the electrostatic interactions between

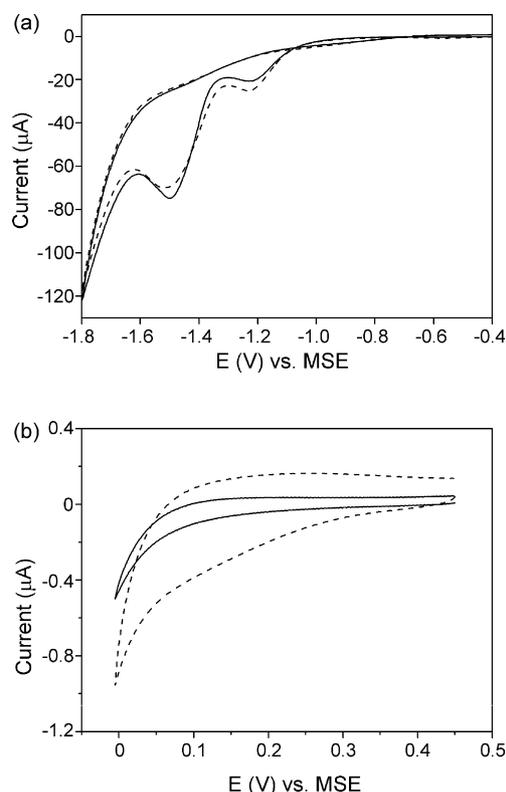
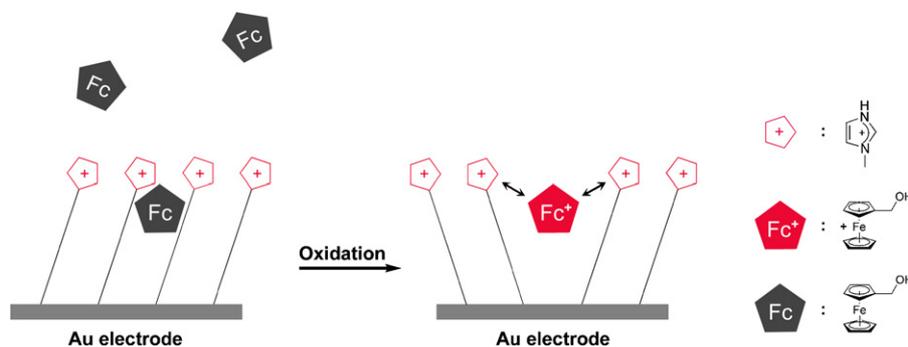


Fig. 6. CVs of (a) reductive desorption in aqueous 0.1 M KOH solution and (b) underpotential deposition of copper in the solution containing 5 mM Cu_2SO_4 and 0.1 M H_2SO_4 on the fresh SAM of 1-(12-mercaptododecyl)imidazole (solid line) and on the SAM-modified gold after cyclic potential scans in the acidic solution of ferrocenemethanol (dashed line).



Scheme 3. Schematic diagram for the proposed disorder of the SAM by incorporated ferrocenemethanol. Ferrocenemethanol wedges itself into the SAM and increases the distance between positively charged imidazoles.

incorporated ferrocenemethanol and charged imidazole shown in Scheme 3. Neutral hydrophobic ferrocenemethanol may be incorporated into the SAM similarly to the adsorption of surfactants on the SAMs [25,26]. Ferrocenemethanol can act as a wedge into the SAM because the oxidation of the incorporated ferrocenemethanol causes the electrostatic repulsion between the oxidized ferrocenemethanol and protonated imidazoles of the SAM, leading to the disorder of the SAM. Facile access to the electrode through the disordered SAM may cause the enhanced outer-sphere electron-transfer through the SAM, while the SAM still blocks the access of Cu^{2+} . The tilt of the SAM may explain the increased capacitance and the conserved in-plane interaction.

3.3. Electron transfer behaviors of cationic redox-active probe, $\text{Ru}(\text{NH}_3)_6^{3+}$, on the electrode presenting the SAM of 1-(12-mercaptododecyl)imidazole

For further examination of the electrochemical property of the SAM of 1-(12-mercaptododecyl)imidazole, we performed other electrochemical experiments with a cationic redox-active probe, $\text{Ru}(\text{NH}_3)_6^{3+}$, instead of anionic $\text{Fe}(\text{CN})_6^{3-}$. When CV was performed on the freshly prepared SAM on gold, completely irreversible CVs in the solution containing $\text{Ru}(\text{NH}_3)_6^{3+}$ were observed in both pH 2 (Fig. 7a) and pH 12 (Fig. 7b). These results clearly indicate that attractive force between redox-active probes and the

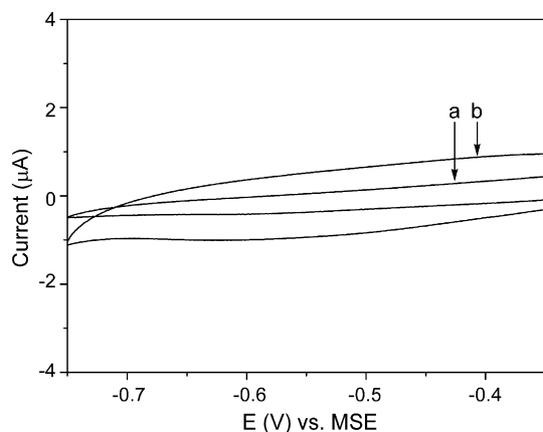


Fig. 7. CVs of $\text{Ru}(\text{NH}_3)_6^{3+}$ solution (a) in the acidic electrolyte and (b) in the basic electrolyte on the SAM-modified electrode.

electrode is a key factor in enhancing the electron transfer.

In addition to the electrostatic force, adsorption of molecules is another factor to control the electron transfer. $\text{Fe}(\text{CN})_6^{3-}$ adsorbs and desorbs reversibly on the SAM of imidazole depending on the pH (*vide supra*). When the SAM electrode was soaked in the acidic solution of $\text{Fe}(\text{CN})_6^{3-}$ to immobilize $\text{Fe}(\text{CN})_6^{3-}$, quasi-reversible voltammetric behavior on this $\text{Fe}(\text{CN})_6^{3-}$ immobilized SAM was observed in acidic solution containing $\text{Ru}(\text{NH}_3)_6^{3+}$ (Fig. 8a). In contrast, dramatic decrease in electron transfer in basic solution containing $\text{Ru}(\text{NH}_3)_6^{3+}$ (Fig. 8b) indicates that the adsorbed $\text{Fe}(\text{CN})_6^{3-}$ desorbs in basic solution. To desorb $\text{Fe}(\text{CN})_6^{3-}$ completely, CV was performed independently in acidic electrolyte containing $\text{Ru}(\text{NH}_3)_6^{3+}$ (Fig. 8c) after the $\text{Fe}(\text{CN})_6^{3-}$ immobilized SAM was immersed in 0.1 M KOH solution. The resulting electrode retained the completely irreversible behavior in redox reaction of $\text{Ru}(\text{NH}_3)_6^{3+}$.

Based on these results, it could be concluded that the adsorption of $\text{Fe}(\text{CN})_6^{3-}$ onto the protonated imidazole had great effect on the electrochemical property. To elucidate the role of the adsorbed $\text{Fe}(\text{CN})_6^{3-}$, we hypothesize two possibilities: (1) the adsorption of $\text{Fe}(\text{CN})_6^{3-}$ induces the formation of pin-

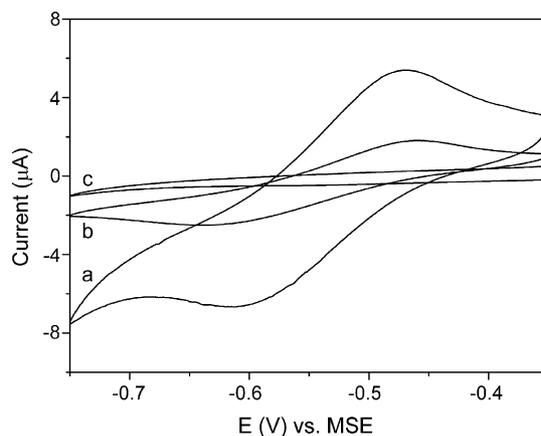


Fig. 8. CVs of $\text{Ru}(\text{NH}_3)_6^{3+}$ solution in the (a) acidic and (b) basic electrolyte on the SAM-modified electrode after immersion in the acidic solution containing $\text{Fe}(\text{CN})_6^{3-}$ and (c) in the acidic electrolyte on the SAM-modified electrode after immersion basic solution following the treatment in the acidic solution containing $\text{Fe}(\text{CN})_6^{3-}$.

holes in the SAM called “ion channel”, and (2) the redox-active molecules such as $\text{Ru}(\text{NH}_3)_6^{3+}$ coordinates with the adsorbed $\text{Fe}(\text{CN})_6^{3-}$ in a second ionic layer on the SAM and shuttles electrons [9]. The first hypothesis can be rejected by the slow electron transfer (data not shown) when $\text{Fe}(\text{CN})_6^{3-}$ was replaced with other redox-inactive molecules such as $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, PF_6^- , and $\text{Cr}(\text{CN})_6^{3-}$. The second hypothesis also cannot explain our system because XPS data showed no evidence of the residual $\text{Ru}(\text{NH}_3)_6^{3+}$ on the adsorbed $\text{Fe}(\text{CN})_6^{3-}$ in a second ionic layer. Neither of two hypotheses can explain our system well. Another possible explanation would be the facile access of $\text{Ru}(\text{NH}_3)_6^{3+}$ to the electrode. The adsorbed $\text{Fe}(\text{CN})_6^{3-}$ is reduced to $\text{Fe}(\text{CN})_6^{4-}$ during the potential sweep for CV of $\text{Ru}(\text{NH}_3)_6^{3+}$ because its reduction potential is higher. Many polyvalent cations associate with $\text{Fe}(\text{CN})_6^{3-}$ in aqueous solutions forming ion-pairs [27]. In addition, Scherer et al. reported that reduced $\text{Fe}(\text{CN})_6^{4-}$ forms a stronger inner sphere complex with highly charged cations than oxidized $\text{Fe}(\text{CN})_6^{3-}$ [28]. Though XPS showed no evidence of this ion-pairs, the reduction of the adsorbed $\text{Fe}(\text{CN})_6^{3-}$ may increase the positive charge leading to the higher interactions between surface-bounded $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+}$ in the solution. This interaction may allow $\text{Ru}(\text{NH}_3)_6^{3+}$ to approach to the $\text{Fe}(\text{CN})_6^{4-}$ layer, leading to the fast electron transfer.

4. Conclusions

We have studied the electrochemical properties of the SAM of 1-(12-mercaptododecyl)imidazole. Surface $pK_{1/2}$ determined by faradaic impedance titration using anionic $\text{Fe}(\text{CN})_6^{3-}$ as a redox probe was 7.3. The electrochemical property of the SAM was investigated by the following procedures: (1) CV in the solution containing $\text{Fe}(\text{CN})_6^{3-}$ with repeated alternation of pH values to confirm the electrostatic interactions of the protonated or deprotonated imidazole with $\text{Fe}(\text{CN})_6^{3-}$, (2) CV in the acid or basic electrolyte containing $\text{Ru}(\text{NH}_3)_6^{3+}$ as a cationic redox probe to verify the effect of the polarity of a redox probe, and (3) investigation of the electrochemical property of the SAM-modified electrode pre-soaked in the solution containing $\text{Fe}(\text{CN})_6^{3-}$ to detect the effect of the adsorption and the desorption of a redox probe on the surface. Experimental results indicated that the SAM of 1-(12-mercaptododecyl)imidazole experienced the reversible protonation/deprotonation of imidazole depending on pH of the solution, which caused the reversible adsorption/desorption of negatively charged $\text{Fe}(\text{CN})_6^{3-}$. The adsorption of charged $\text{Fe}(\text{CN})_6^{3-}$ enhanced the electron transfer of both $\text{Fe}(\text{CN})_6^{3-}$ itself and other redox-active molecule such as $\text{Ru}(\text{NH}_3)_6^{3+}$. This electrochemical behavior of the SAM of 1-(12-mercaptododecyl)imidazole suggests that properties of SAMs can be tailored by the chemical and electrochemical treatments after the formation of the SAM.

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