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Electrochemical Oxidative Adsorption and Reductive Desorption of the Self-Assembled Monolayer of Decanethiol on Au(111) Surface in KOH Ethanol Solution

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Abstract

The electrochemical characteristics of an Au(111) electrode were investigated in 0.1 M KOH ethanol solutions containing various concentrations of decanethiol. Anodic and cathodic peaks corresponding to the oxidative adsorption and reductive desorption, respectively, of a self-assembled monolayer (SAM) of decanethiol were observed. Both peaks negatively shifted with the increase in the thiol concentration by ca. 57 mV/decade, showing that the redox process is a one-electron process. The adsorbed amount determined from the charge corresponding to the reductive desorption increased with an increase in the decanethiol concentration but never reached the saturated amount as long as the cyclic voltammograms were continuously recorded with the sweep rate of 10 – 200 mV s-1. It increased with the holding time at +0.1 V, which was much more positive than the anodic peak potential, and reached the saturated amount in ca. 10 min in the 10 μM thiol solution. The reductive peak potential also negatively shifted with the holding time but for a longer period. It kept shifting for ca. 60 min in the 10 μM thiol solution, which is much longer than the time when the adsorbed amount reached the saturated value. These results suggest that the formation of a highly ordered SAM requires a much longer time than the adsorption of the thiol.

Introduction

Self-assembled monolayers (SAMs) of alkanethiols on a gold surface have attracted many research groups because of their wide variety of potential applications [1-3]. Stable monolayers can be very easily formed by soaking a substrate in a solution containing alkanethiols. The self-assembly is achieved by a chemical bond formation between the substrate atoms and sulfur atoms of the thiols and the hydrophobic interaction between the alkyl chains. The formation process and the structure of the thiol SAMs on Au(111) have been studied in detail by various techniques including IR [4,5], quartz crystal balance (QCM) [6,7] and scanning tunneling microscopy (STM) [8-10]. It is now well known that the alkanethiols are arranged in striped structures when the coverage is low [8-10] and in a $(\sqrt{3} \times \sqrt{3})R30°$ or $c(4\sqrt{3} \times 2\sqrt{3})$ structure with a tilt angle of 30° from the surface normal when the coverage becomes high [11]. STM also revealed that there are many defects in the SAMs such as missing rows and pits [12-14]. The missing-row-defects are attributed to the orientational and translational domain boundaries, and the pits were revealed to be vacancy islands (VIs) of the gold atoms. We have found that the density of the pits is strongly dependent on the solvent [15] and temperature [16] employed for the self-assembly.

After Widrig et al. reported that alkanethiolates are desorbed from the gold surface by the following one-electron reduction process in an alkaline aqueous solution [17]:

$$\mathrm{Au-SR} + e^{-} \Rightarrow \mathrm{Au} + \mathrm{RS}^{-} \qquad (1)$$

many electrochemical studies of the reaction (1) have been carried out because the peak area and the shape of the cathodic peak for the reductive desorption and its peak potential provide useful information of the SAM such as the adsorbed amount, stability, adsorption energy, orientation, and substrate morphology [17-36]. For example, it was found that the longer the alkylchain, the more negative the reductive peak potential, reflecting the stronger van der Waals attractive interaction among alkylchains [17]. The reductive desorption process has been investigated by many techniques including electrochemistry [17-26], FT-IR [27-29], electrochemical QCM [30-32], and *in situ* STM [33-36]. Several groups suggested the formation of an "aggregate" or "micelle" near or on the electrode surface after the reductive desorption of the SAM [28,33,35]. We have also carried out the *in situ* STM investigation of the reductive desorption process of the hexanethiol SAMs on an Au(111) surface both in H_2SO_4 and KOH aqueous solutions and found that the desorption of the SAMs was initiated from the defects of the SAM, i.e., missing rows and the edge of the vacancy islands, and the desorbed thiolate molecules formed aggregates in H_2SO_4 but the reconstructed, i.e., clean, surface of Au(111) was observed after the desorption of the SAM in KOH solution [36]. When the electrode potential is scanned back in the positive direction after the reductive desorption of the alkanethiolates, an anodic peak corresponding to the oxidative readsorption of some of the desorbed alkanethiolates, i.e., the reverse reaction of the reductive desorption reaction given by the reaction (1), is observed.

The oxidative adsorption of alkanethiolates on a gold surface can be used to form the thiol SAM and has been also studied electrochemically [37,38] as well as with EQCM [31, 32, 39] but much less compared with the reductive desorption.

In this work, we have studied the electrochemical characteristics of an Au(111) electrode in ethanol solutions containing various concentrations of decanethiol. Size and position of the anodic and cathodic peaks corresponding to the oxidative adsorption and reductive desorption, respectively, of the decanethiol SAM are used as probes for the amount and order, respectively, of the SAM. The experimental results clearly show that the adsorption of the thiol took place much faster than the ordering of the SAM.

Experimental Section

Decanethiol ($CH_3(CH_2)_9SH$: $C_{10}SH$) from Wako Pure Chemicals, ethanol (Wako Pure Chemicals), and KOH (Aldrich) were all reagent grade chemicals and were used as received. High purity Ar gas was purchased from Air Water. Gold single crystals were prepared by Clavilier's method [40] from a gold wire (>99.95 %, ø = 0.8 mm, Tanaka Precious Metal). An Au(111) face was used as a substrate for the electrochemical measurements and was prepared as follows. The gold single crystal was cut in parallel to the (111) facet, mechanically polished using 0.5 µm diamond slurry and then annealed in air at 800 °C for ca. 8 h. The Au (111) surface was flame-annealed in a hydrogen flame, gradually cooled under nitrogen stream prior to each measurement, and then transferred to a three compartment electrochemical cell.

The electrochemical measurements were carried out in 0.1 M KOH ethanol solution containing various concentrations of decanethiol with the hanging meniscus configuration using a potentiostat (Hokuto Denko, HA-151) and a function generator (Hokuto Denko, HB-111). Cyclic voltammograms (CVs) were recorded using an X-Y recorder (Graphtec, WX1200). The electrode potential was referred to an Ag/AgCl (saturated NaCl) electrode, and the counter electrode was a Pt wire. was employed for the measurements. The electrolyte solution was deaerated by bubbling Ar for 30 min before each experiment.

Results and Discussion

Figure 1 shows the CVs of an Au(111) electrode measured in 0.1 M KOH ethanol solution containing (a) 10 µM, (b) 100 µM and (c) 1 mM $C_{10}SH$. The potential of the electrode was held at around –1.0 V, where the adsorption was not expected, when the electrode surface was placed in contact with the electrolyte solution and then was continuously cycled between +0.1 V and –1.0 V at a scan rate of 20 mV s^{-1}. All the CVs shown in Fig. 1 were recorded after several potential cycles so that the shape of the CVs became unchanged. Consequently, they represent the steady states of the adsorption and desorption of the $C_{10}SH$ molecules in the ethanol solution. The anodic and cathodic peaks corresponding to the oxidative adsorption and the reductive desorption, respectively, were observed in all the cases shown in Fig. 1, but no clear peaks were observed in a solution containing 1 µM $C_{10}SH$. While the peak area decreases by repeating the potential cycle, i.e., desorption/readsorption processes, in aqueous solution containing no thiol because some of the desorbed thiol molecules diffuse away from the electrode surface and are not able to be readsorbed [23,24], the CV recorded under the present conditions did not change with potential cycles.

As summarized in Fig. 2 for the results obtained in 5 different concentrations, both peaks negatively shifted with the increase in the thiol concentration by ca. 57 mV/decade. Similar relations were observed when the sweep rate was varied between 10 – 200 mV s^{-1}. The peak potentials can be estimated by the Nersnt equation assuming that the cathodic and anodic reactions are given by Eq. (1) and its reverse reaction [41].

$$E_{1/2} = E_o^{'} + (RT/F)\ln(a_{C10S\text{-}Au}/a_{C10S}\text{-}a_{Au}) \qquad (2)$$

where $a_{C10S\text{-}Au}$, a_{C10S}-, a_{Au} , are the activities of the SAM, $C_{10}S^-$ in solution and gold. It must be mentioned here that since the pKa of $C_{10}SH$ is ca. 10 [42,43] and pH of the 0.1 M KOH solution is ca. 13, $C_{10}SH$ is fully ionized and exists as $C_{10}S^-$. Because a_{Au} is 1, Eq. (2) can be written for 298 K as:

$$E_{1/2} = E_o^{'} + 0.059\log(a_{C10S\text{-}Au}/a_{C10S}\text{-}). \qquad (3)$$

The thiol SAM is known to have several phases [8,9,10] and $a_{C10S\text{-}Au}$ depends on the phase, i.e., the order of the SAM. Thus, the redox potential should depend both on the thiol concentration and the order of the SAM. If $a_{C10S\text{-}Au}$ is constant, Eq. (3) becomes

$$E_{1/2} = E_o^{'} - 0.059\log(a_{C10S}\text{-}) \qquad (4)$$

and the peak potential is expected to change with thiol concentration by 59 mV/decade. This is in very good agreement with the experimental results presented in Fig. 2, showing the peak positions are controlled mainly by the thiol concentration. This means $a_{C10S\text{-}Au}$ is essentially constant and the oxidative adsorption and reductive desorption of the thiol proceeded as shown in Eq. (1) and its reverse reaction, respectively. This result reflect the fact that the time domains in the present sweep rate dependence measurements (10 mV s^{-1} - 200 mV s^{-1}) are short compared with the time required for the reorganization/ordering of the SAM which leads to the significant change in the $a_{C10S\text{-}Au}$ as shown below.

The charge of the cathodic peak representing the adsorbed amount increased with the thiol concentration as also shown in Fig. 2. They are 54.9, 57.5, 58.9, 63.0 and 65.1 μC cm^{-2} in 10 μM, 50 μM, 100 μM, 500 μM and 1 mM thiol solutions, respectively, and are smaller than 73.3 μC cm^{-2}, which is the expected value for the saturated coverage, i.e., (√3 x √3)R30° structure [44-48]. The value of 73.3 μC cm^{-2} has been reported for the reductive desorption of the SAM formed externally in an ethanol solution containing only the thiol [23,24].

These results suggest that the scan rate of 20 mV s^{-1} was too fast for the monolayer of full coverage to be formed. Thus, the formation rate was followed by measuring the area of the cathodic stripping peak as a function of the holding time at +0.1 V where the thiol adsorption takes place. The electrode was placed in contact with the 0.1 M KOH ethanol solution containing 10 μM $C_{10}SH$ at –0.9 V where no adsorption takes place then scanned by 20 mV s^{-1} to +0.1 V where the adsorption is expected to occur. After holding the potential at +0.1 V for a certain time period, the potential was negatively scanned until a cathodic peak was observed. Figure 3 shows the linear scan voltammograms obtained after the potential was held at +0.1 V for (a) 0, (b) 10 and (c) 60 min. It is clear that the peak area increased and peak position shifted negatively as the holding time increased. More detailed results of the holding time dependencies of the position and charge of the cathodic peak are shown in Fig. 4. The charge sharply increased with the holding time from 54.9 μC cm^{-2} at 0 min, i.e., under continuous scanning, to 73.3 μC cm^{-2}, the saturated amount, at 10 min. This result confirms that the saturated coverage was not reached during the continuous scanning because the scan rate was too fast [46].

The peak position negatively shifted with time, showing that $a_{C10S\text{-}Au}$ decreased with time. In other words, the stability of the SAM, i.e., attractive interaction among the adsorbed thiol, increased with time. It is very interesting that the peak position kept shifting even after the saturated coverage was reached and became constant after 60 min at ca. –1.02 V. These results of time dependencies of the amount and position of the cathodic peak suggest that although the full coverage is reached within 10 min, the order of the SAM at this stage is low and a highly ordered SAM is formed after the reorganization and ordering of the SAM, which requires a much longer time of ca. 60

min. Similar results were obtained by impedance [37] and EQCM [39] measurements for the SAM formation under potential control as well as for the SAM formation without potential control in solutions containing only the thiol [4,6,8,9]. Thus, we can conclude that the reorganization/ordering of the SAM is not affected by applied potential.

If the sufficient time was allowed for the oxidative deposition of the SAM, both the charge and the position of the reductive desorption peak were independent of the thiol concentration, ca. 73.3 μC cm^{-2} and ca. –1.02 V, respectively, although the time required to reach these values depended on the thiol concenration. This means the reductive peak potential is no longer given by Eq. (3) when the monolayer of the highest order is formed and equilibrium between the SAM and thiolate ion in solution is not attained during the desorption process.

More detailed investigations for wider ranges of concentration and sweep rates as well as using other techniques such as impedance and potential pulse are now under way.

Conclusion

The electrochemical oxidative adsorption and reductive desorption of a self-assembled monolayer (SAM) of decanethiol on an Au(111) electrode in 0.1 M

KOH ethanol solutions containing various concentrations of decanethiol were investigated. Both anodic and cathodic peaks corresponding to the oxidative adsorption and reductive desorption, respectively, of the SAM negatively shifted with the increase in the thiol concentration by ca. 57 mV/decade, showing that the redox process is the one electron process. The adsorbed amount determined from the charge corresponding to the reductive desorption increased with the increase in the thiol concentration but never reached the saturated amount as long as the cyclic voltammograms were continuously recorded with the sweep rate of 10 – 200 mV s^{-1}. By holding the electrode potential at +0.1 V, where the adsorption of the thiol is expected, the area of the reductive desorption peak, i.e., the amount of adsorbed thiol, increased and the peak position negatively shifted with the holding time. While the adsorbed amount reached the saturated value at ca. 10 min in the 10 μM thiol solution, the peak position kept shifting until ca. 60 min in the same solution, suggesting that the formation of a highly ordered SAM requires a much longer time than the adsorption of the thiol.

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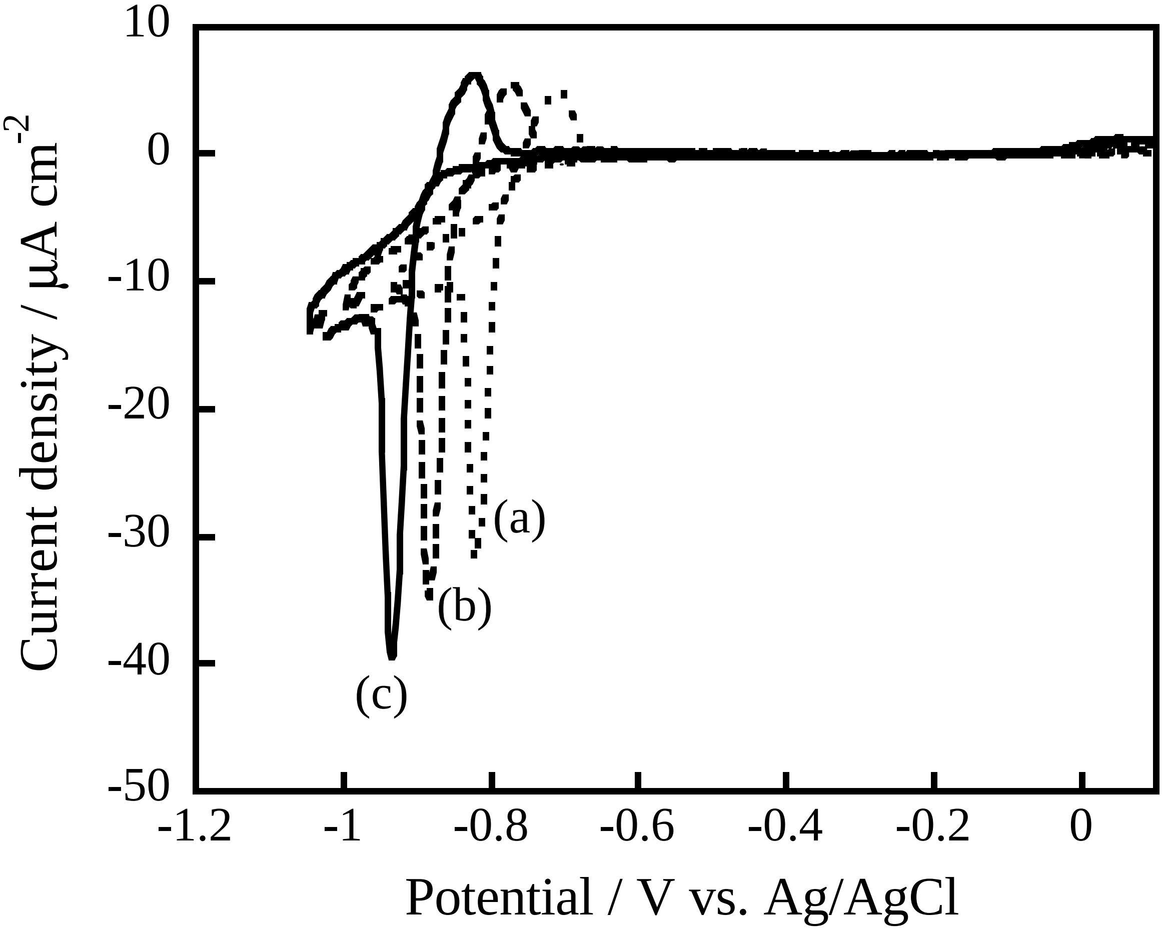
Figure Captions

Figure 1. Cyclic voltammograms of the Au(111) electrode measured in 0.1 M KOH ethanol solution containing (a) 10 µM, (b) 100 µM and (c) 1 mM $C_{10}SH$. Scan rate: 20 mV s^{-1}.

Figure 2. The anodic (●) and cathodic (■) peak potentials and the amount of the adsorbed thiol calculated from the charge of the cathodic peak (○) as a function of the $C_{10}SH$ concentration in 0.1 M KOH ethanol solution.

Figure 3. Cyclic voltammograms of the Au(111) electrode measured in 0.1 M KOH ethanol solution containing 10 µM $C_{10}SH$ after holding the potential at + 0.1 V for (a) 0, (b) 10, and (c) 60 min. Scan rate: 20 mV s^{-1}.

Figure 4. The cathodic peak potential (●) and the amount of the adsorbed thiol determined from the charge of the cathodic peak (■) as a function of the holding time at + 0.1 V in 0.1 M KOH ethanol solution containing 10 µM $C_{10}SH$.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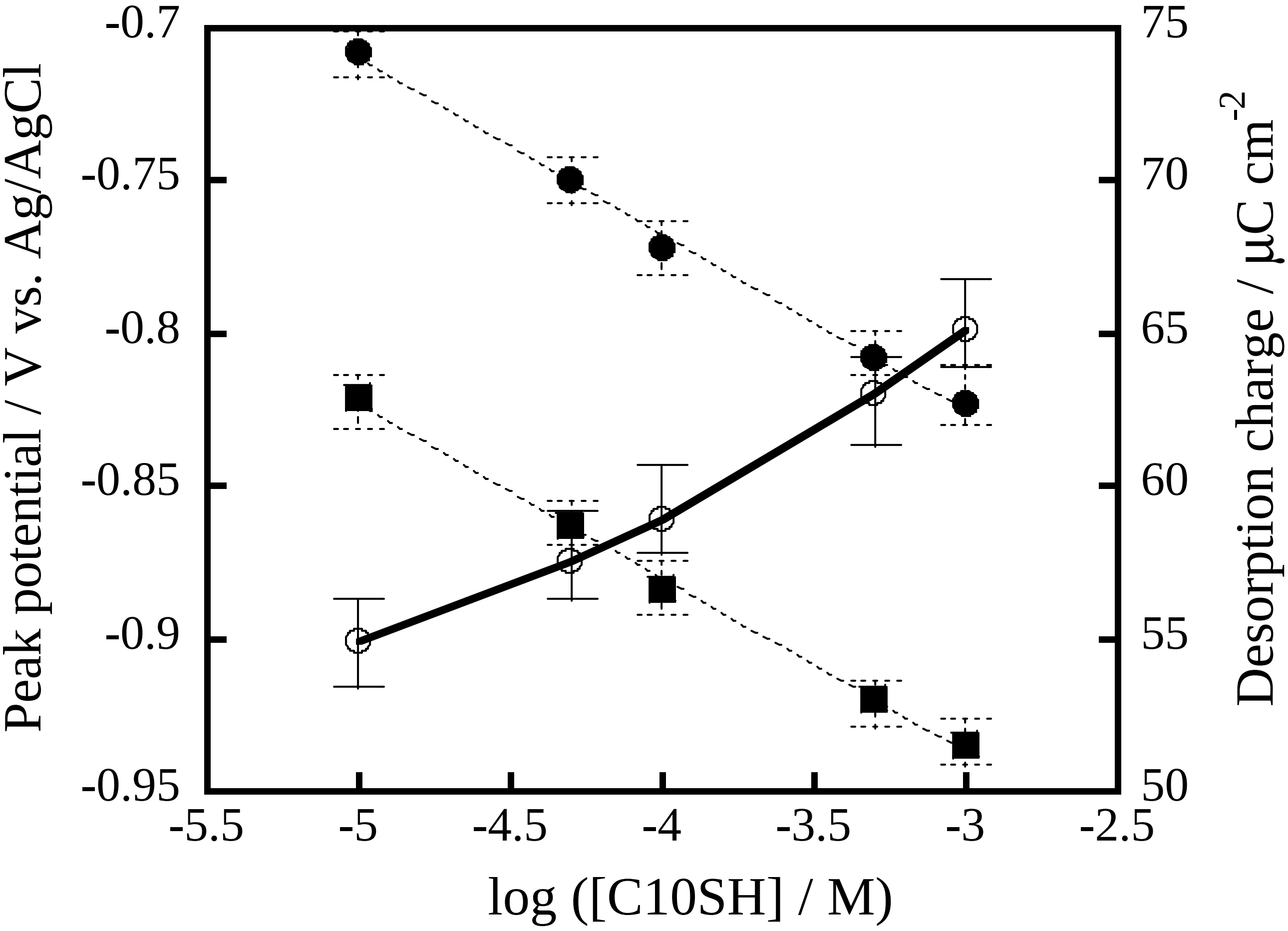
-10
-20
-30
-40
-50
-1.2
-1
-0.8
-0.6
-0.4
-0.2
0
Current density / μA cm^{-2}
Potential / V vs. Ag/AgCl
(a)
(b)
(c)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-0.8
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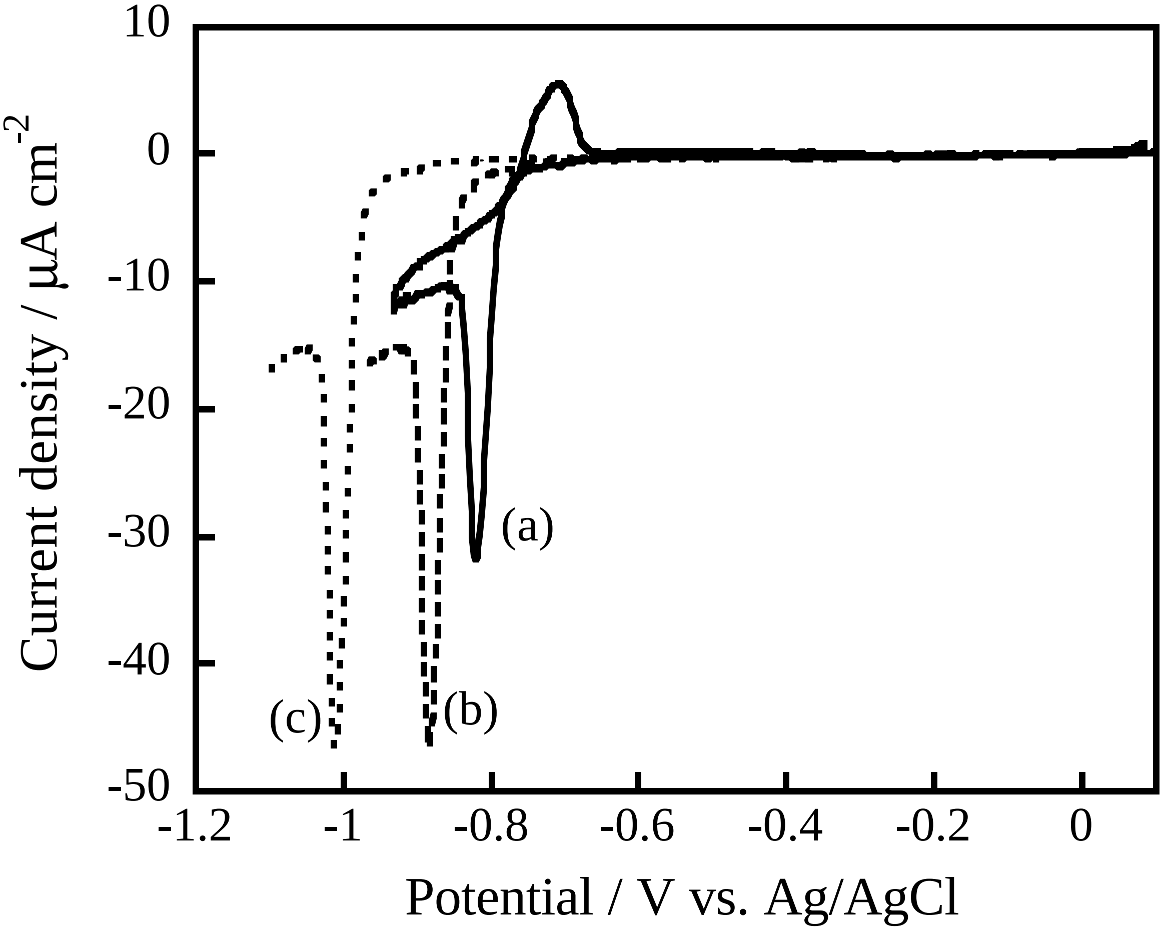
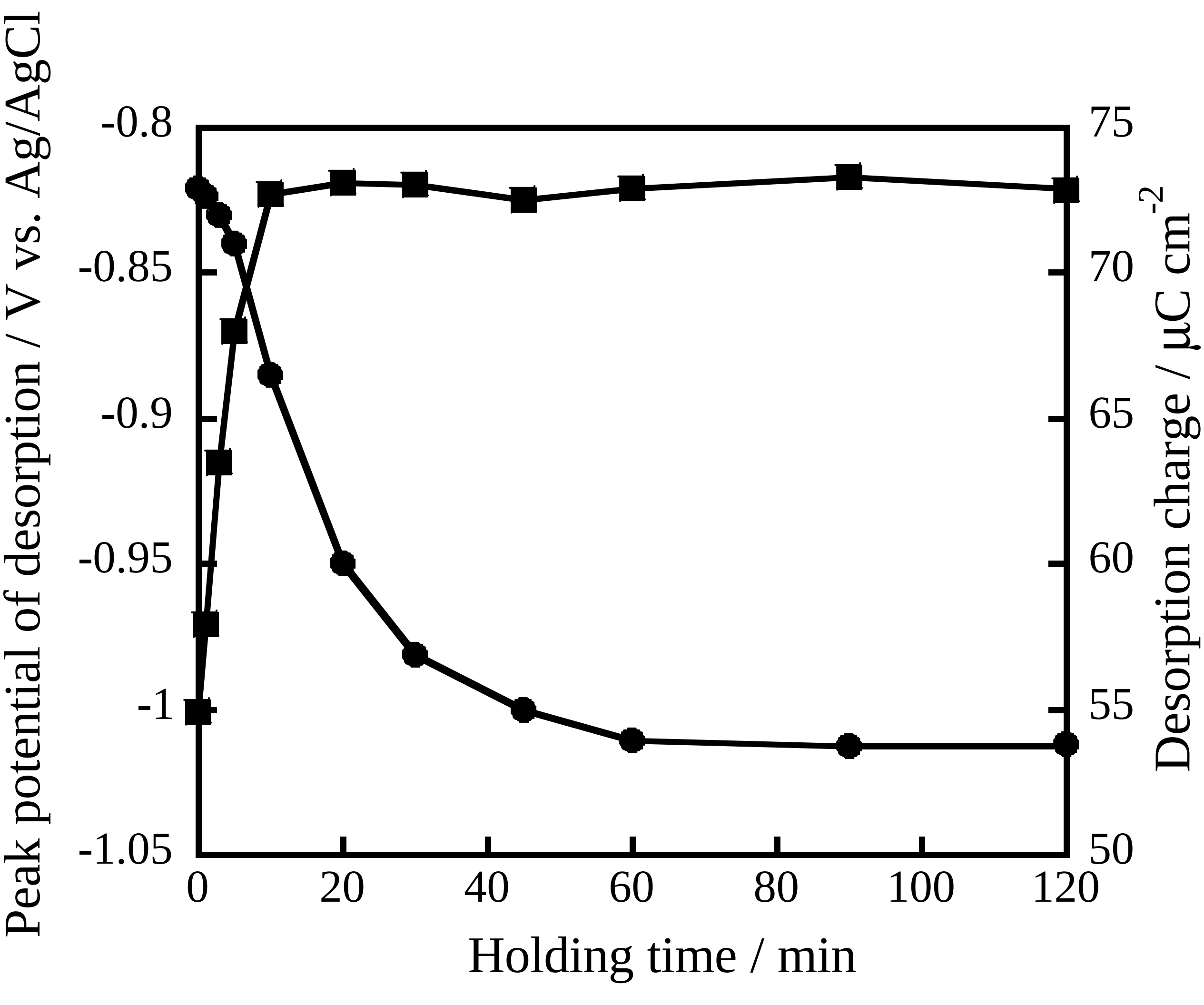
-0.9
-0.95
75
70
65
60
55
50
-5.5
-5
-4.5
-4
-3.5
-3
-2.5
Peak potential / V vs. Ag/AgCl
Desorption charge / μC cm^{-2}
log ([C10SH] / M)


10
0
-10
-20
-30
-40
-50
Current density / μA cm-2
-1.2
-1
-0.8
-0.6
-0.4
-0.2
0
Potential / V vs. Ag/AgCl
(a)
(b)
(c)


Peak potential of desorption / V vs. Ag/AgCl
-0.8
-0.85
-0.9
-0.95
-1
-1.05
Desorption charge / μC cm^{-2}
75
70
65
60
55
50
0
20
40
60
80
100
120
Holding time / min