Thermal effect on the voltammogram of 7-ferrocenycarbonyloxy-1-heptanethiol self-assembled monolayer

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Abstract

The voltammetry of self-assembled monolayers (SAMs) of 7-ferrocenycarbonyloxy-1-heptanethiol ($FcCO_2(CH_2)_7SH$) has been studied as a function of temperature. Such SAMs are, when oxidised, susceptible to loss of ferrocene via nucleophilic attack, but at temperatures only just above room temperature, there is an accelerated loss of ferrocene from the chain termini, an increase in the capacitance of the layer in its reduced state and a positive shift in the $E_{1/2}$ value is observed. A comparison between these data and the effects of multiple scans recorded at room temperature suggests that there is a re-orientation, induced at slightly elevated temperatures, which is associated with the ferrocene ester linkage at the chain terminus and which apparently renders ferrocene more susceptible to nucleophilic attack. With the increasing of temperature, the loss of ferrocene (terminal) is accelerated, due to the capacitances and permeability of the SAM layers. The positive shift of the $E_{1/2}$ value is harder to interpret but may result because the ferrocene is in more intimate contact with the layer and is placed in a more hydrophobic, less polar environment. Other possible influences on the shift of $E_{1/2}$ are discussed. This work confirms that electroactive terminal groups can provide information on the microenvironment at the SAM/electrolyte interface through variations in current and potential.
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1. Introduction

The extraordinary order of alkanethiol self-assembled monolayers (SAMs) chemisorbed on gold has provoked intense interest [1–3] in using them to study effects of distance, order, packing and chemical environment on heterogeneous electrode transfer events. SAMs based on alkane thiols ($CH_3(CH_2)_nSH$) represent a versatile means for the modification of surfaces [4–6]. The SAM can be tailored to have a specific thickness or to present, at the SAM/solution interface, a given physical (such as hydrophobicity or hydrophilicity) or chemical property (for example a specific chemical group able to react with or bind to another chemical entity) [5,7–14,19,21]. One aspect of this versatil-

ity has been the attachment of redox active groups (especially terminal ferrocene group) at the SAM/solution interface as a means for the study of electron transfer as a function of distance, since the separation between electrode and redox group may (in theory) be controlled and varied simply and accurately [1,4,6,8,26–32]. Studies of these systems (typically with the redox active group prepared in a mixed monolayer with methyl terminated thiols) have also focussed on a range of other physico-chemical aspects of these layers [2,11,14,22,34–48]. Especially relevant to this work is the fact that the electrochemistry of these systems could also convey information about the microenvironment of the ferrocene or other redox group and hence, by inference, some structural or environmental aspects of the monolayer and how it depends upon, for example, the redox state [14,35–37]. For ferrocene, the transformation from a neutral terminal group in its reduced state, to a positively charged group when in its oxi-

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dised state (ferricinium) should be disfavoured by a less polar environment [4,8,14–21,23–25]. Such an environment may be created if the ferrocene group buries itself into the layer, or if it is in a mixed monolayer and is surrounded by methyl terminated alkane thiols with longer chain lengths [35,37]. An important aspect of SAMs and highly relevant to their proposed uses, how was the layer quality and properties depend on temperatures and their phase behaviours. Although there were early studies of this aspect of SAMs [45,46] phase transitions of, or the effect of temperature on, SAMs has received less attention than many other aspects, but the importance of an understanding of the effects of temperature in this area is becoming increasingly recognised. Organised assemblies of organic molecules such as SAMs or lipids undergo melting and other transitions at moderate temperatures and methods such as the current due to redox probes [51] quartz crystal microbalance, Raman spectroscopy [48] and reflection absorption infrared spectroscopy (RAIRS) [53] have all been used to examine aspects of the effects of temperature on SAMs of different types, both in solution and in air or vacuum. In this paper, we present the results of an investigation of the thermal effects on the electrochemistry of a ferrocene terminated alkane thiol. In particular, the variations of current as temperature increases afford a general insight into the changes that occur within a layer on heating. Variations of potential are harder to interpret but offer some supplementary information.

2. Experimental

2.1. Chemicals

Perchloric acid (70%), ferrocene carboxylic acid (97%), 1,6-dibromohexane (96%) were purchased from Aldrich Chemical Company and used without further purification to prepare the electrolyte solutions with dionize water (resistivity, >18.2 MΩ cm) respectively. The 7-ferrocenycarbonyloxy-1-heptanethiol ($FcCO_2(CH_2)_7SH$) is synthesized using ferrocene carboxylic acid and 1,6-dibromohexane.

2.2. Instrumentations

The voltammetry performed in this study employed a conventional three-electrode cell with a polycrystalline gold as a working electrode, Pt wire as a counter electrode and Ag/AgCl (satd. KCl) as a reference electrode. The commercial potentiostat an electrochemical quartz crystal microbalance (EQCM, Shin EQCN1000, Korea) was used for all electrochemical investigations. Electrodes were gold on 10 MHz AT-cut quartz crystals, which were usually used for EQCM. The gold used was 99.99% pure and vacuum (ca. 1×10^{-7} Torr) deposited on 5 nm Ti under-layer to form a Au-layer of ca. 100 nm thickness by Thermal & E-beam evaporation system (HVEB 200, Hanvac, Korea.).

2.3. Electrode cleaning and preparation

All electrodes were pre-treated and polishing by repeated cycling (50 mV s^{-1}) of the electrode in 0.1 M H_2SO_4 between the system's O_2 and H_2 evolution potentials, until a reproducible voltammogram with well defined features was obtained. The gold evaporated crystals were cleaned thoroughly by Piranha solution (a mixture of 98% H_2SO_4 and 30% H_2O_2 at 2:1 v/v) [Caution! Piranha solution is a very strong oxidising agent and reacts violently with organic compounds. Freshly prepared piranha solution should be handled with extreme care]. The average roughness factor and surface areas were calculated for lab made polycrystalline gold electrode 1.2 ($\pm$0.10) and 0.26 cm^2 respectively.

The cleaned gold polycrystalline electrode was modified by dip-treatment in a CH_2Cl_2 (99.9% HPLC grade, Aldrich) solution containing $FcCO_2(CH_2)_7SH$ at 24 h. After modification of the substrates, it was rinsed thoroughly with pure CH_2Cl_2 and then dry with stream of N_2. Then the $FcCO_2(CH_2)_7SH$ monolayer modified crystal was monitored with EQCM. A thermal controlled oven (OF-22GW, JEIO Tech, Korea) was used to achieve thermal control of the cell. The electrochemical cell was operated between 25 and 70 °C using a thermostat controller and a period of 20 min was allowed for the system to reach equilibrium at each temperature. Copper under potential deposition (upd) [30] onto electrodes covered with the layer showed no significant defects in the layer. Copper upd was used to provide access to the potential region where there would be no overlap with current from monolayer oxidation.

3. Results and discussion

Electrochemical observation (specially cyclic voltammetry) is studied in 0.1 M perchloric acid (at various scan rates) at room temperature. Before the variation of voltammetry with temperature is examined, it is necessary to present the voltammetry of layers at room temperature. Reported voltammograms for ferrocene-terminated thiols do vary in their detail; for example there are suggestions of broadened electrochemical features possibly due to inhomogeneous sites [2], whereas others have observed shoulders and spikes in the voltammetry [33]. Part of the reason for this variation is the fact that different laboratories use different electrode surfaces, pre-treatment regimes and layer preparation methods. In this study, there was also some variability between layers, seen in the occasional observance of a shoulder on the positive going scan of the voltammogram at a potential below that of the anodic peak. This variability between layers in this study may be due to the different polycrystalline EQCM gold electrodes employed. Fig. 1 shows voltammograms as a function of scan rate for the $FcCO_2(CH_2)_7SH$ [Cu under potential deposition (upd)] SAM on Au surface. There is a broadening of the anodic peaks at the higher scan rates, much more
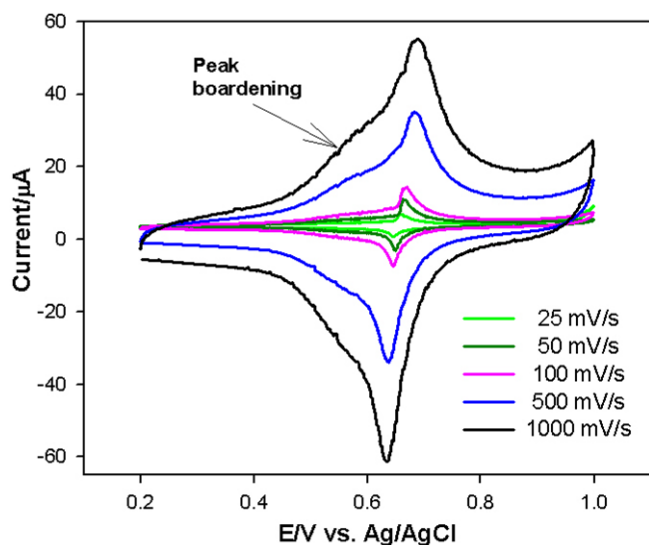
Fig. 1. Cyclic voltammograms for a $FcCO_2(CH_2)_7SH$ in 0.1 M perchloric acid as a function of scan rate. Scan rates were 50, 100, 500 and 1000 mV s^{-1}.

so than for the cathodic peaks. These reflect the unfavourable environment created by the array of neighbouring positive charges when the termini are converted to ferricinium. As was generally observed, there is very less apparent broadening on the cathodic peak. In attempting to interpret this data, some information concerning the structural state of the layers maybe helpful. Sato et al. [36] monitored formation of $FcC_{11}SH$ layers by PM-FTIR and used analysis of the peak positions of the methylene stretching modes to conclude that the order of their layers lay between that of a solid and a liquid and increased with adsorption time of the thiol so that after 15 h the layers approached the order of the solid state. Although no comparable study seems to have been carried out for $FcCO_2(CH_2)_7SH$, the longer time should ensure that films are in a comparable state. Sato et al. [36] also reported that increased formation time led to chain orientations that grew closer to the surface normal. Aside from the initial state of the layers, another issue that is relevant for these systems is whether or not there is any structural change resulting from the oxidation and consequent introduction of positive charges at the SAM/electrolyte interface. Popenoe et al. [33] using IRRAS on $FcCOOC_{11}SH$ layers reported no detectable changes in the orientation of the polymethylene chains as a function of applied voltage, whereas Shimazu et al. [35] used a combined FTIR/EQCM method on $FcC_{11}SH$ (11-ferrocenyl-1-undecanethiol) to suggest that the layer shows less tilt when oxidised but attributed this discrepancy to a difference in surface packing between their work (0.9×10^{14} molecules cm^{-2}) and that of Popenoe et al. (2.8×10^{14} molecules cm^{-2}), stating that for a layer as well packed as the latter, no re-orientation would be expected upon oxidation. With these factors in mind, the peak boardening may reflect a region of the surface perhaps possessing different packing or order and

it is possible that the oxidation leads to greater homogeneity as a result of Coulombic repulsion. The peak boardening may represent a region of solid-like monolayer, while the majority of the layer is in a more liquid-like state. If electron transfer occurs via tunnelling, then a more ordered solid-like state should make tunnelling easier, by virtue of fewer defects in the methylene chain. Such defects can have a dramatic effect on tunnelling [6]. Upon oxidation, the Coulombic repulsion between neighbouring ferricinium groups may cause more disorder and create uniformity of the layer and when this repulsion is removed, there is relaxation back to the original state on a timescale of a few seconds, because the peak was seen to be present on subsequent scans.

It is studied the influence of several scanning on $FcCO_2(CH_2)_7SH$ self-assembled monolayer stability and its properties. An important point that emerges from studies of ferrocene derivatives and ferrocene terminated thiols (especially from solution studies of ferrocenes) is that the oxidised form of ferrocene, ferricinium, is susceptible to nucleophilic attack (by OH^-, Cl^-, NO_3^- and other nucleophiles) [50] with, in the case of ferrocene thiols with the ester linkage, possible subsequent cleavage of the link leading to loss of ferrocene [33]. This last observation is from unpublished work in slightly basic solutions of chloride. Therefore, for ferrocene thiol SAMs there is a loss of activity with the time spent in the oxidised form and hence a decreased charge for oxidation seen in the voltammogram after repetitive cycles. The effect is found to be least pronounced for perchloric acid electrolytes at low pH, hence the use of that electrolyte in these studies. Since an objective of this work was to examine the voltammetry as a function of temperature, which entails repetitive scanning, a brief discussion of the effect of multiple voltammograms on stability is presented here.

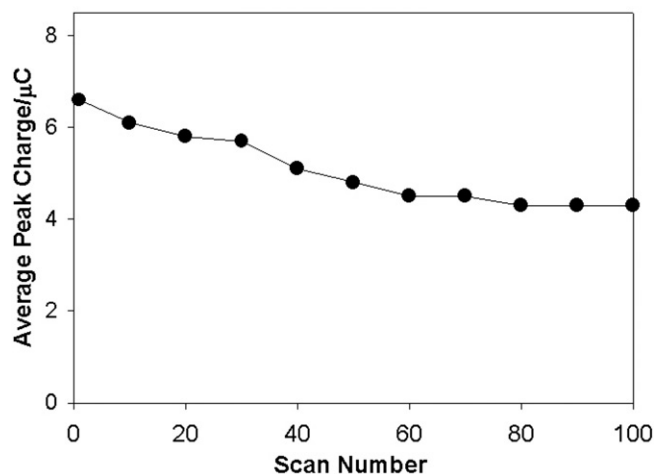Fig. 2 presents a plot of the decline of the average peak charge with scan number for a $FcCO_2(CH_2)_7SH$ typical of

Fig. 2. Average peak charges as a function of scan number for a $FcCO_2(CH_2)_7SH$ SAM. Scans were carried out between 0.2 and 1.0 V at 50 mV s^{-1} in 0.1 M $HClO_4$ at room temperature.

those used in this work. After 100 cycles (representing about 15 min spent in the oxidised form), the charge has fallen to 38% of its original value. In addition to the decrease in charge, the peak potentials (not shown) showed no significant increase even after about 25 cycles but then a slow consistent increase with extended cycling with the total increase being 0.21 mV for the anodic peak over a total of 100 cycles (equivalent to the time period shown in figure). There was no significant variation in the cathodic peak potential observed over the same time. Another important measurement made during these experiments was the capacitative charging current, measured at 0.3 V when the layer is in its reduced form. This value showed no change within experimental error. This observation suggests no significant change in the layer. There may be a small decrease of layer thickness because of loss of ferrocene. However, the layer may pack more effectively after the bulky terminal groups are lost. Since the blocking properties remain largely unaffected, despite the significant loss of charge, the view that the loss of charge is a result of ferrocene lost to nucleophilic attack is reinforced. Copper upd

stripping indicated that no free gold sites were available on the surface even after this repetitive cycling, confirming no loss of thiol overall.

Charge and current variation are studied under the influence of temperature on voltammetry. As noted above, there was some variability in the voltammetry of the thiols studied, namely the occasional presence of a shoulder on the positive scan. A similar variability was also seen in these temperature dependent studies, but experimental observations were generally consistent on all the layers studied. Fig. 3 presents voltammograms for $FcCO_2(CH_2)_7SH$ SAM of Au (Cu upd) layer at four different temperatures. There are several features of note. First, the peak currents fall as the temperature increases. This is partly a result of repetitive cycling leading to loss of attached ferrocene. Secondly, we observe a shift in the anodic peak potential towards more positive values as the temperature increases in Fig. 3(A)–(D). The cathodic peak potential shifts to more negative values and the net effect of these changes is a positive shift in $E_{1/2}$. Finally, the height on the peak disappears as temperature increases.
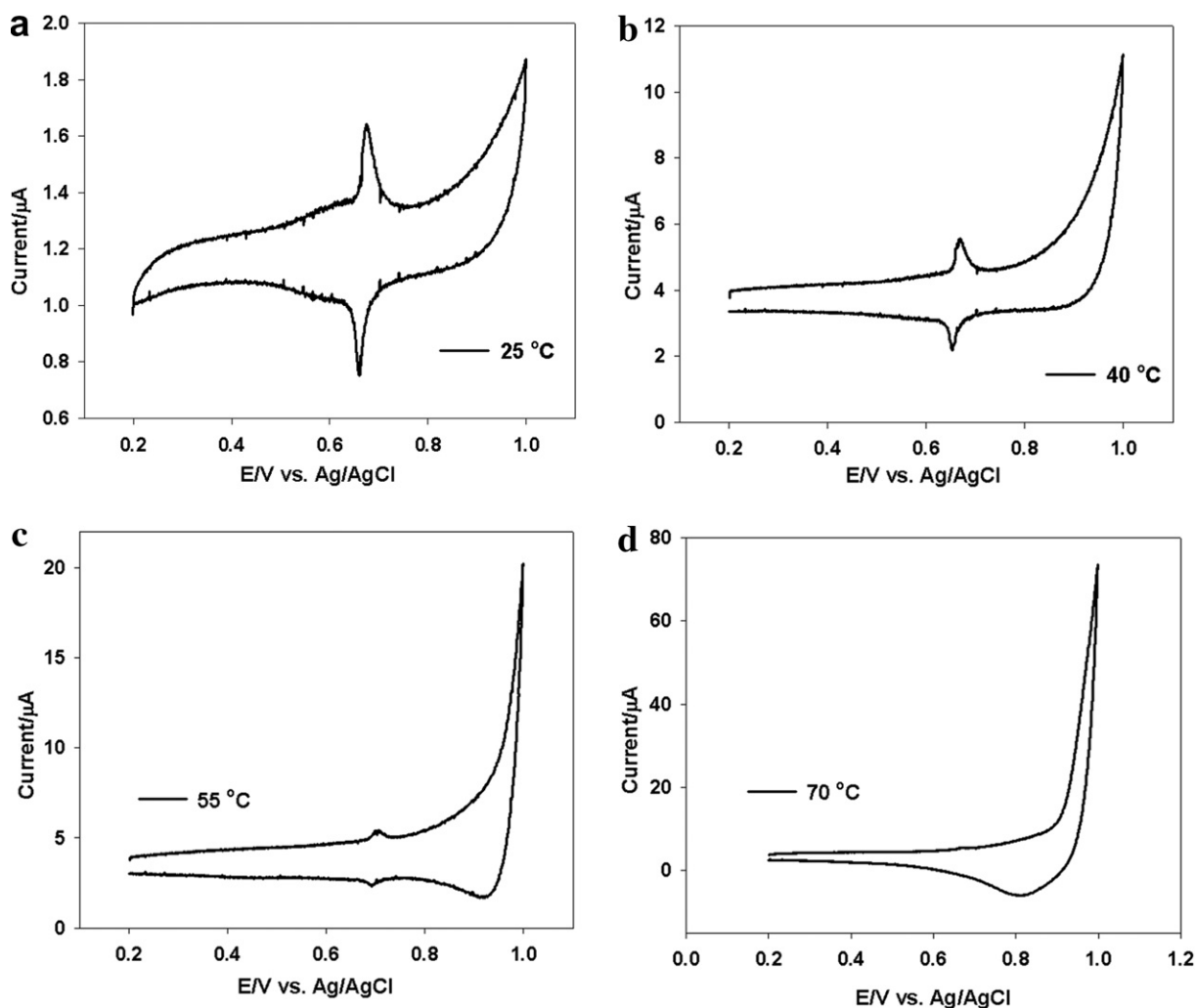

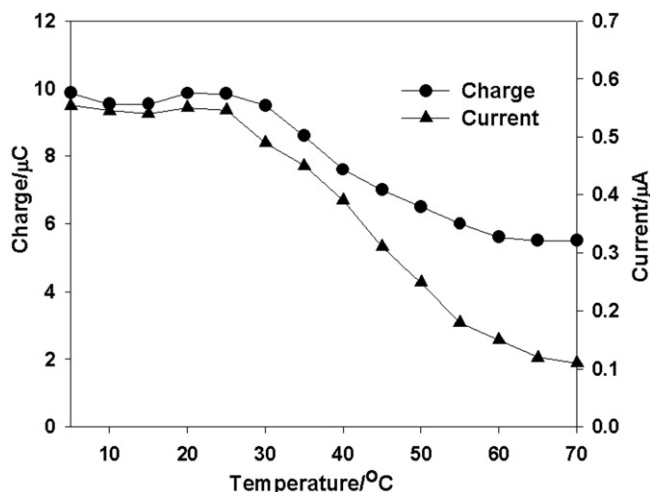Fig. 3. Cyclic voltammograms for a ferrocene terminated SAM, $FcCO_2(CH_2)_7SH$, at 25, 40, 55 and 70 °C. Scans were at 50 mV s^{-1} in 0.1 M $HClO_4$.

Fig. 4. Plots of current and charge as a function of temperature for the FcCO$_2$C$_7$SH. Data taken from voltammograms like those shown in Fig. 3.

Fig. 5. Variation of $E_{1/2}$ with temperature for a layer of FcCO$_2$(CH$_2$)$_7$SH. Data taken from voltammograms like those shown in Fig. 3.

In order to assess the reasons for these changes, a number of different parameters were examined to see how they were affected by temperature. First, a plot of the average (of oxidation and reduction) charge and current as a function of temperature is shown in Fig. 4. Both quantities follow a similar trend, with a roughly constant region in the range from 5 to about 25 °C (the currents show a slight increase, but this is more a result of the loss of the terminal ferrocene and thus a redistribution of the current). Above around 25 °C, both charge and current fall consistently with further increases in temperature. The overall decline in both quantities was about 68% and 80% respectively. The upd results were remarkably reproducible over a series of experiments. This is consistent with an irreversible loss of ferrocene from the surface during the course of the experiment but no loss of thiol from the surface of the electrode. The consistency and reproducibility of the upd data in several different experiments indicate that possible loss of thiol at elevated temperatures and subsequent replacement by adventitious impurities is extremely unlikely. With regard to the mechanism of ferrocene loss, an extensive discussion is beyond the scope of this paper, but it is likely to occur via anion attack at ferrocene according to the solution phase findings of Prins et al. [50]. Hydrolytic cleavage has been reported for ferrocene thiols with the ester linkage but in slightly basic solutions [33].

Peak potential variations are measured the influence of temperature on cyclic voltammetry. Further insight into the changes that occur as a function of temperature can be found from the variation of $E_{1/2}$ during similar experiments. This is depicted in Fig. 5. There are some broad similarities between the trends seen in this figure and those in Fig. 4. First, there is very little change up to a temperature of 20 °C, but there then follows an increase as the temperature increases to 65 °C and then the difference remains relatively constant for the remainder of the heating cycle. If the layer is cooled, there is a small decrease in $E_{1/2}$ (not
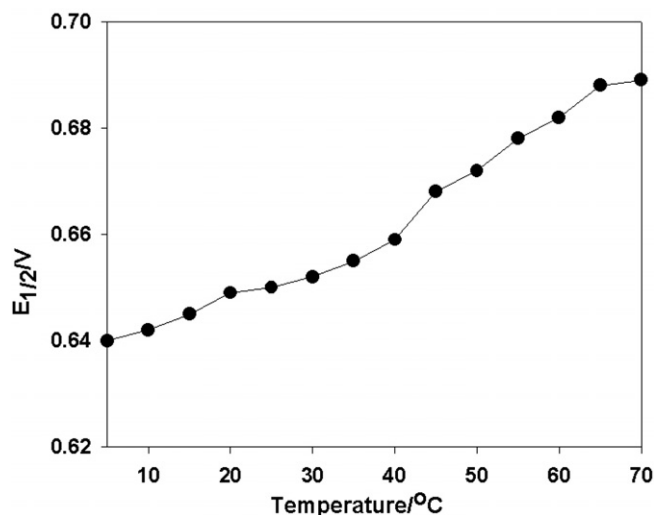
shown) but it does not return to its original value. This trend in $E_{1/2}$ to more positive values is, at first glance, contrary to expectation. Chidsey et al. [2] studied mixed monolayers of FcCO$_2$(CH$_2$)$_{11}$SH and CH$_3$(CH$_2$)$_9$SH and observed a positive shift of the peak potentials (which appears to be about 0.08 V as estimated from Fig. 2 in their paper) as the mole fraction of FcCO$_2$(CH$_2$)$_{11}$SH increased from 0.1 to 1.0. Since ferrocene is lost as temperature increases here, these data suggest that a *negative* shift of $E_{1/2}$ would be seen. As around 60% of the ferrocene is lost a shift of the order of +0.064 to +0.069 V might be expected. However, Creager and Rowe [37] examined the effect of neighbouring chain length in mixed monolayers of ferrocenylhexane thiol and CH$_3$(CH$_2$)$_n$SH. As n increased and the neighbouring chains provided a more hydrophobic environment for the ferrocene terminal group, the peak potentials became more positive, from 0.34 V for $n = 3$ to 0.65 V for $n = 9$. The surrounding alkyl chains create an environment where the uncharged ferrocene form of the layer is favoured and the oxidised, charged ferricinium is less stable, thereby shifting the potential to more positive values. It is likely that both these effects make a contribution to the changes seen here and this point will be discussed further below after supplemental experimental data has been described.

The challenge in evaluating the data is to separate the effects of loss of ferrocene with cycling from the effects of temperature on the FcCO$_2$(CH$_2$)$_7$SH SAMs. The changes in current and charge principally reflect loss of ferrocene, whereas the shifts in potential are influenced by both factors. The capacitative current for the layer in its reduced form is helpful in providing information on temperature effects alone, since it is invariant with repetitive cycling. It also helps to indicate any loss of thiol. Considering the information in this way allows a reasonable picture of the effects of temperature to be deduced despite the absence of any spectroscopic or structural data.

As noted earlier, there is little structural work that has been reported for ferrocene terminated thiols, but the limited data available suggest that for this chain length the layers should be close to solid-like, as deduced from comparisons of the methylene stretching vibrations [36]. However, comparisons between papers are fraught with complications arising from different electrodes, electrode preparation methods, layer preparation methods and so on. As well as a relative lack of structural data on ferrocene thiols at room temperature, there has been less attention paid to the effects of temperature on alkane thiol SAMs. However, this area is slowly growing in interest. Badia et al. [47] examined $CH_3(CH_2)_nSH$ layers (where n varied from 16 to 20) through the variation of current from the reduction of $Fe(CN)_6^{3-}$ and reported two increases in permeability for each layer. These were compared with well-known permeability profiles for di-n-acylphosphatidylcholines, which undergo gel–liquid transitions and untilting/rippling transitions. They observed current increases and current maxima attributed to the co-existence of tilted and untilted chains and to the co-existence of melted and unmelted chains. This was suggested to produce transient dislocations or boundaries at the interfaces between those co-existing regions leading to enhanced permeability to the redox probe and hence to increased current. Teuscher et al. [48] used the QCM and SERS to study temperature effects on tetradecanethiolate and reported a rotator-like transition (a gradual process involving formation of gauche defects in the surface methyl and methylene units) and a melt-like transition at 70 °C. More recently, Bensebaa et al. [49] examined RAIRS to investigate the temperature behaviour of n-alkanethiols on gold over a substantial temperature range. They report a general trend where there is a gradual untilting of the alkyl chain as well as the appearance of gauche defects near the surface. These effects are almost reversible but then a large number of defects located below the surface were observed as temperatures exceeded 350 K for a C_{20} layer and these changes were found to be irreversible. They also suggested that layers comprised of shorter chain lengths, below C_{12}, were more disordered than the longer chains and did not study these systems. The bulky ferrocene terminal group is likely to make the layers used here less well ordered, especially since at the beginning of the experiments the entire layer is comprised of ferrocene thiols. Thus we may view the layer used here as moderately well ordered but less well ordered than chains of comparable length with a methyl termination. As the temperature is increased defects at chain termini or various phase transitions might occur.

When the loss of ferrocene with extended cycling is considered, it is instructive to compare the loss as a function of scan number for the extended cycling experiment and the same data for the variation with temperature. As was apparent in Fig. 4, there is little decline in the range 5–25 °C but then an accelerated decline is particularly apparent. It is hard to quantify the effect of temperature on the expected rate of loss of ferrocene, but an expected Arrhe-

nius type of behaviour would not give the response seen in the figure, which suggests an accelerated loss of ferrocene above about 25 °C. These facts suggest that there may be a change occurring in the layer at this temperature (or in a range between 20 and 30 °C). The consequences of this seem to be twofold. First, the layer becomes a little more permeable to ions, hence the increase in double layer capacitance in the reduced form and secondly, the ferrocene is apparently more susceptible to nucleophilic attack and its subsequent removal. This accounts for the acceleration of the loss of ferrocene once this temperature is reached although there will be, of course, an effect attributable to the influence of temperature on this process.

The loss of ferrocene is, however, at odds with the shift in the $E_{1/2}$ value to more positive potentials as the coverage decreases. A negative shift of potential would be expected when the repulsions between neighbouring electroactive groups are lessened by the loss of ferrocene [2]. To rationalise this, we must consider two things. First, electrode potentials are temperature dependent, the variation of potential with temperature being a classical means by which the entropy of the process may be determined. Recent work on ferrocene in acetone over a range of temperatures [51] while not directly relevant, indicates that the shifts observed here could reasonably be ascribed to an effect of temperature on potential alone, which would indicate an increased entropy change upon oxidation as temperature increases. However, the fact that the overall change in the $E_{1/2}$ is likely to be a composite of a negative shift due to the lower repulsion as coverage decreases and a positive shift from the effect of temperature on potential suggests that there may well be another contribution shifting the $E_{1/2}$ positive. This could happen, as we have seen, if the ferrocene group encounters a more hydrophobic or less polar environment [37]. Thus it is likely that a contribution to the shift in potential arises from a change in the orientation of the ferrocene group such that it is either forced into the layer, or is in more intimate contact with it. This would have the effect of stabilising the ferrocene form at the expense of ferricinium, thus shifting the potential to a more positive value. The situation is complex and other factors which may influence the potential change include changes in the screening of the ferricinium charges as the double layer alters with temperature and ion pairing, although better ion pairing would shift the potential in a negative direction. These and other aspects have been discussed in more detail elsewhere [25,52,53].

The question then remains, what sort of change is occurring in the $FcCO_2(CH_2)_7SH$ SAMs with Cu upd? From the data of Badia et al. [47] on alkane thiols of lengths C_{16} to C_{20} an extrapolation would suggest that the tilting/untilting and gel/liquid phase transitions, if present for these layers, would occur at temperatures below those where a transition is observed here. In addition, the shorter chain lengths and presence of ferrocene make the layers less well ordered in the first instance than those studied by Badia et al. So, it is unlikely that these transitions are being seen

here. However, since an accelerated loss of ferrocene is observed, there may a structural change at chain termini involving the ferrocene–ester linkage with the result that the ferrocene is more susceptible to nucleophilic attack and is also in an environment that is less polar (shifting the potential to more positive values). Because of the involvement of this group there is not necessarily a correlation between the temperature for transitions observed on methyl-terminated layers of similar length and that observed here. If ferrocene is forced into the layer, there may also be a resulting slight increase in the capacitance of the film if the chains are forced apart, which would account for the change in capacitance of the layer observed as a function of temperature. It is interesting to note that the fact that this structural change appears to occur at around room temperature or very slightly above it may be part of the reason for some of the variability of response noted here between different layers and may also be responsible for the shift of $E_{1/2}$ to more positive values when extended cycling was carried out at room temperature.

4. Conclusions

Self-assembled monolayer of $FcCO_2(CH_2)_7SH$ is studied under different temperatures. Despite the loss of ferrocene with cycling, temperature variation studies and careful examination of changes in a number of voltammetric features reveals information about the environment of the ferrocene group and how it changes with temperature. The data suggest that the ferrocene–ester linkage undergoes a shift in its orientation at temperatures in the range 20–25 °C, which results in the easier removal of the group by nucleophilic attack and which also places ferrocene groups that are not removed in a more hydrophobic environment, rendering their oxidation more difficult. The fact that this change occurs very close to room temperature may account for some of the variation between voltammograms seen here and those reported in the literature. This emphasises the importance of developing an understanding of the influence of temperature on the properties of $FcCO_2(CH_2)_7$ SH SAMs of all types.

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