

Jutta Scharf · Hans-Henning Strehblow
Björn Zeysing · Andreas Terfort

Electrochemical and surface analytical studies of self-assembled monolayers of three aromatic thiols on gold electrodes

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Abstract Three thiols with three aromatic rings and different structure – terphenyl-4-methanethiol (TPMT), terphenyl-4-thiol (TPT), and anthracene-2-thiol (AT) – have been used to form self-assembled monolayers (SAM) on vapour-deposited and flame-annealed Au films on glass substrates. All three SAMs effectively block the anodic formation of Au oxide, indicating densely packed layers which prevent the access of water and hydrated ions through the organic layer to the metal surface. The film improves its inhibiting properties with duration of exposure to the thiol solutions, reaching completion after 1 hour [1]. The charge-transfer reaction of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ system is blocked for TPMT films with an insulation of the π -electron system from the Au surface by the methylene group. TPT and especially AT films show the current density of the redox reactions. It is proposed that the charge transfer occurs via the aromatic molecules of the SAMs to the Au surface.

Keywords SAM · Aromatic thiols · Electronic conductivity · Redox reactions

Introduction

The electronic conduction of organic molecules is an essential property in biology and possibly for future technological applications [2, 3]. A significant example is

vitamin A (retinol) which is formed by oxidative splitting of β -carotene and is an essential part of rhodopsin which, in turn, plays an important role in the physiological processes of optical vision. Adsorption of gases increases the conductivity of molecules like β -carotene which suggests their active role for the sense of smell [4]. Conducting polymers are discussed as materials for electronic parts to obtain further miniaturisation of electronic devices down to the size of single molecules [5]. Although the conductivity of organic molecules is extremely important for many processes in life sciences and their possible technical application for sensors and electronic parts, little is as yet known about this property. Since the direct measurement of molecular conductivity is a very complicated process [6], conductivity measurements of thin films are often used as an approximation. Unfortunately, thin films formed by the common spin-on technique usually do not give precise answers to mechanistic questions, because the molecules arrange in an irregular way in these films. The rate-determining step of the effective mechanism could be the conductance along the molecules or, more likely, the electron transfer between molecules, and molecules and contacting metal electrodes [7]. The distances between molecules determine the charge transfer rate between them. As these distances and orientations are arbitrary, no detailed mechanistic conclusions may be taken from the integrating measurements of the conductivity of these films. As a consequence, a well-ordered orientation of the related molecules is required, this is realised in self-assembled monolayers (SAMs) [8]. If suitable molecules, such as alkanethiolates, are attached to an electrode surface by chemical bonds and are well oriented to each other, they lead to an insulation of the metallic substrate from the adjacent electrolyte. The inhibition of various electrochemical reactions like oxide formation, metal dissolution, or charge transfer with redox systems within the electrolyte by SAMs of alkanethiols is a well known example [9, 10]. Various methods have been applied to characterize the structure of SAMs of alkanethiols like ellipsometry [11], X-ray diffraction [12],

J. Scharf · H.-H. Strehblow (✉)
Institut für Physikalische Chemie und Elektrochemie,
Heinrich-Heine Universität Düsseldorf,
Universitätsstrasse 1, Gebäude 26/42,
40225 Düsseldorf, Germany
E-mail: henning@uni-duesseldorf.de/
aterfort@chemie.uni-hamburg.de
Tel.: +49-211-8114867
Fax: +49-211-8114842

B. Zeysing · A. Terfort
Institut für Anorganische und Angewandte Chemie,
Universität Hamburg, Martin-Luther-King-Platz 6,
20146 Hamburg, Germany

X-ray absorption spectroscopy [13], and scanning tunneling microscopy (STM) [14] to mention only a few examples from the extensive literature. Usually these thiols form a compact $\sqrt{3}\times\sqrt{3}$ R30° structure on an Au (111) single crystal substrate with the molecules oriented upright to the surface and their sulfur atoms bound to the three-fold hollow side of the Au surface [8].

For thiols with an appropriate molecular structure, one may expect electron transfer from the electrolyte via the molecules to the metal substrate. With this path for the electron transfer one has a chance to learn about the electronic conductance of single molecules. SAMs of aromatic thiols on noble and semi-noble metals like gold, silver, or copper provide an interesting possibility to realise this concept. To learn about the electronic conduction across SAMs, three thiols with conjugated π -systems – terphenyl-4-methanethiol (TPMT), terphenyl-4-thiol (TPT), and anthracene-2-thiol (AT) (Fig. 1) – have been synthesised and bound to Au electrodes. These modified electrodes have been studied by electrochemical methods, providing a first insight into the conducting properties of these films. The arrangements of the molecules relative to the surface have been controlled by surface analytical studies like angular resolved X-ray photoelectron spectroscopy (AR-XPS).

This concept is promising also in the light of recent publications. Biphenylthiols form SAMs with a similar $\sqrt{3}\times\sqrt{3}$ R30° dense structure according to STM studies [15]. They also isolate the Au substrate from the electrolyte [16] although redox reactions at SAM-covered Au electrodes may occur [17]. Recent *ab initio* calculations for the interaction of phenylthiol with Au clusters suggest an ohmic contact with electronic conduction across the metal-thiol interface with an orientation of this molecule to the Au surface similar to the situation found for other thiols [18].

Materials and methods

The three aromatic thiols used in this study were synthesised using published procedures [19, 20]. Dodecanethiol (DT) was purchased

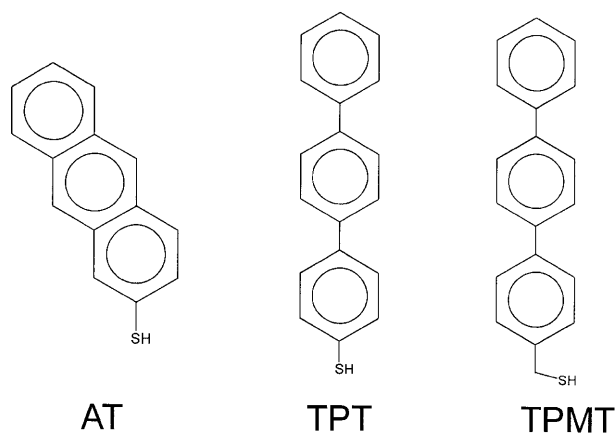


Fig. 1 Structure of the thiols: terphenyl-4-methanethiol (TPMT), terphenyl-4-thiol (TPT), anthracene-2-thiol (AT)

(Sigma-Aldrich Chemie GmbH) and used as received. SAMs formed of DT, which have a blocking characteristic to most electrochemical reactions, were used for comparison. Au electrodes were made by vapour deposition on glass substrates. Glass slides were cleaned in ethanol in an $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ mixture, rinsed with pure water, and finally introduced into the high vacuum of a metal evaporator (Univex 300, Leybold) and sputter cleaned with argon. A 0.5 nm vapour-deposited layer of Cr provided a better adhesive strength for the finally deposited 50 nm gold layer. Immediately before use these gold electrodes were flame-annealed at ca. 700 °C which led to a cleaning and a better surface structure of the preferentially (111) oriented Au crystallites [21]. These electrodes were introduced into 0.001 M solutions of the thiols in tetrahydrofuran. Usually an exposure of 20 min was sufficient to obtain a dense layer with complete coverage that was controlled by the inhibition of the electrochemical formation of Au oxide. For AT an exposure time of 60 min was necessary to obtain an optimum inhibition of the Au surface. Prior to the electrochemical investigations the electrodes were rinsed with deionised water. To investigate the charge transfer at the surface of these modified Au electrodes a solution of 0.005 M $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ was used in electrolytes of different pH. All solutions were prepared with analytically pure substances and deionised water (Millipore water purification system). The stability and performance of the SAMs were studied in 0.1 M $\text{NaClO}_4 + 0.001$ M HClO_4 of pH 2.2 and 0.1 M borax buffer of pH 9.3, the charge transfer in 0.5 M $\text{Na}_2\text{SO}_4 + 0.005$ M $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.005 M $\text{K}_4[\text{Fe}(\text{CN})_6]$. The potentiodynamic polarisation curves of pure and modified Au electrodes were performed with a potentiostat (Schram, Düsseldorf) within a conventional electrochemical cell equipped with a reference and a Pt-counter electrode. $\text{Hg}/\text{Hg}_2\text{SO}_4/1$ M Na_2SO_4 ($E = 0.68$ V) served as reference electrode. All electrode potentials are given relative to the standard hydrogen electrode (SHE). AR-XPS studies were performed in a commercial spectrometer (ESCALAB 200X, VG Instruments). The spectra were taken with a constant pass energy of 20 eV for the spherical sector analyser (Marc 2). For ellipsometric measurements the ellipsometer of Rudolph Instruments was used.

Results and discussion

XPS measurements confirm the presence of thiol layers. The C/S signal ratio increases with increasing take-off angle which proves the position of C on top of the S of the thiol group as expected for an orientation of the molecule with the thiol group as the binding site to the electrode surface. It is further known that the stiff oligophenylenethiols (TPT and TPMT) produce SAMs with a better developed long-range order and possibly better surface-protecting properties. According to NEXAFS and IR studies the benzene rings are tilted towards the surface which causes less stress within the SAM [10]. No details are known about the orientation of AT molecules in the related SAM and investigations with structure sensitive methods are required for any further information. A layer thickness of 13 Å, as determined by ellipsometry, suggests that the molecules are oriented nearly perpendicularly to the surface. Since the three rings in this compound are annelated, they form a single, extended aromatic system which cannot – in contrast to the oligophenylene moieties – be broken by simple rotation around a σ bond.

The well known polarisation curves of pure Au electrodes and those modified with TPT are presented in Fig. 2 for the alkaline and acidic solutions. The pure Au surface shows the formation of Au oxide at $E > 0.8$ V

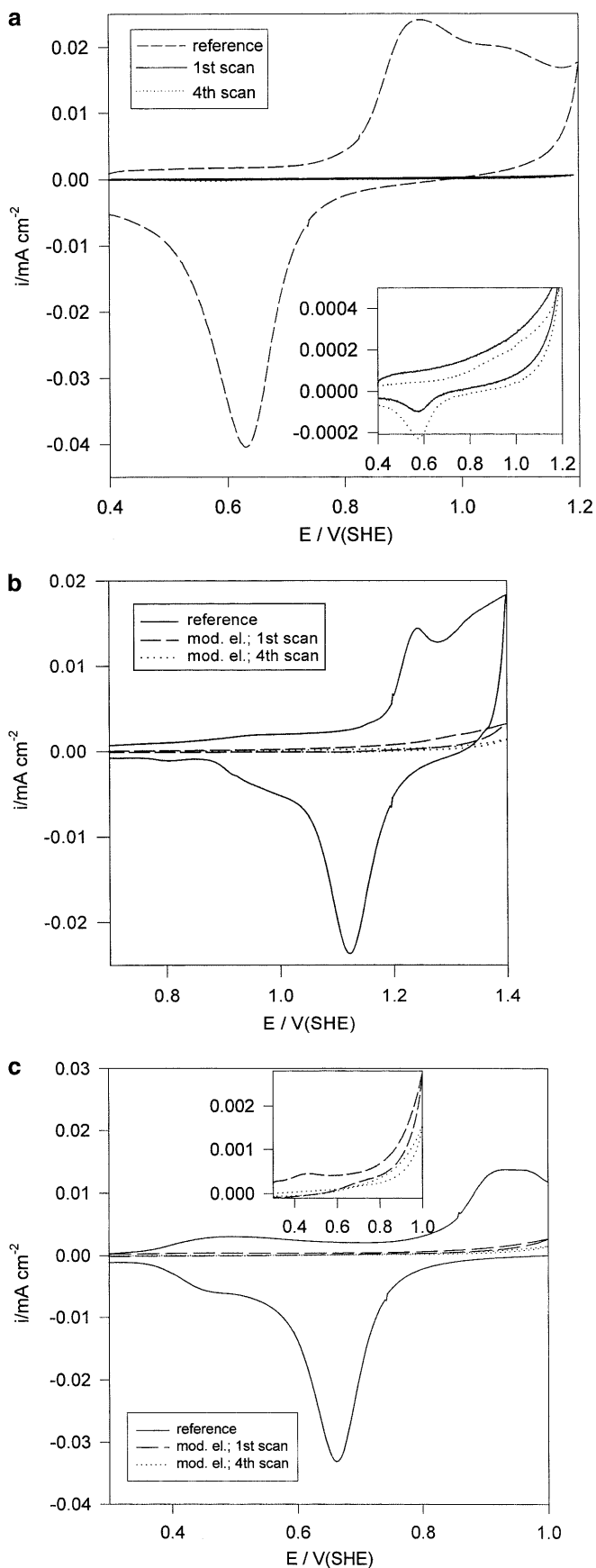


Fig. 2 Potentiodynamic polarisation curve of Au electrodes without (reference) and with inhibition by an SAM of thiol, **a** TPT in borate buffer pH 9.3, **b** TPT in 0.01 M HClO_4 + 0.1 M NaClO_4 , **c** AT in borate buffer pH 9.3

and $E > 1.2$ V for pH 9.3 and 2.2, respectively, with broad peaks at ca. 0.9 and 1.3 V. The related reduction occurs at the cathodic peaks with maxima at 0.63 and 1.1 V, respectively. The potential difference refers to a pH shift of approximately 0.06 V/pH which is expected for thermodynamic reasons. The modification of the surface with TPT suppresses the oxide formation and reduction for both electrolytes (Fig. 2, a, b). Repetitive scans do not show an increase of the current density which demonstrates the stability of the thiol films. Apparently, the thiol monolayer very effectively blocks the anodic oxidation of the Au surface. Similar results are obtained for TPMT and AT (Fig. 2, c). For comparison the charges of the anodic peaks in the range of 0.6 to 1.2 V and of the cathodic peak in the range of 0.9 to 0.3 V are determined in borate buffer of pH 9.3. For a scan from 0.3 to 1.2 V the charge of the modified electrode in both electrolytes is only about 5% of that of the pure Au reference. Repetitive scans lead to a still reliable inhibition of the oxide formation and thus apparently to no damage of the thiol film (Fig. 3). A well inhibited gold surface leads to negligible charges for more than 10 scans. Only if the scan is extended to 1.5 V into the range of oxygen evolution where also the formation of a thick Au oxide film should occur on unprotected parts of the metal surface is an increase of the charge observed. Fig. 4 demonstrates the influence of the immersion time on the inhibition of oxide formation by a TPT layer. The inhibition increases gradually with the immersion time, indicating that the film is still improving up to 1 hour by

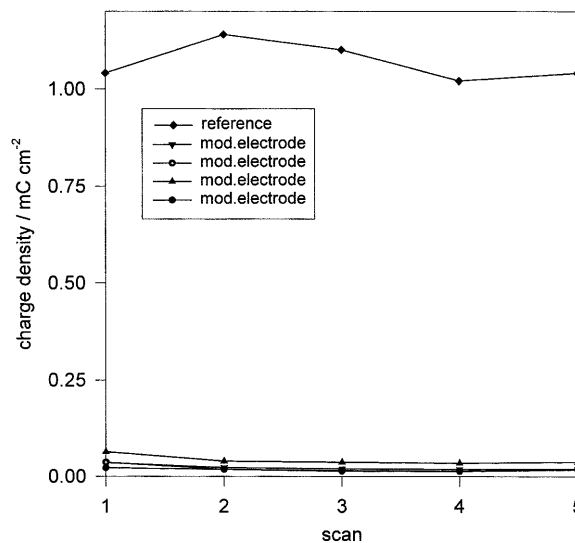


Fig. 3 Anodic charge of Au electrode without (reference) and with inhibition by an SAM of AT in borate buffer pH 9.3 for multiple potentiodynamic scans (scan 10 mV/s, $E = 0.4$ to 1.2 V)

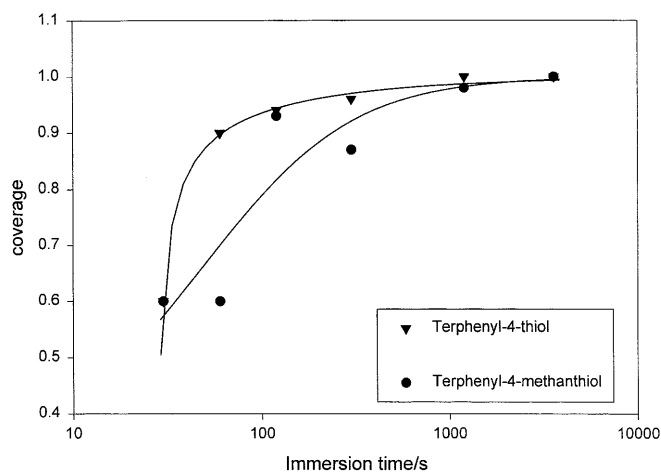


Fig. 4 Charge ratio of Au electrode without (reference) and with SAM (coverage) for potentiodynamic scans 0.4 to 1.2 V, 10 mV/s as a function of immersion time in TPT or TPMT solution

continuous rearrangement and further insertion of additional thiol molecules. Finally, all three thiols form a barrier-type film which prevents the formation of anodic oxide on a gold electrode. Apparently, well-ordered SAMs are dense enough so that water cannot penetrate to the Au surface where its presence is required for oxide growth. Another reaction that might be hindered is the transfer of H^+ ions, which are formed during anodic oxide formation, from the metal surface via the film to the electrolyte. Short immersion times result in still too many defects which allow easy water access to the surface and local oxide growth during the anodic scan and its reduction in the cathodic run.

The polarisation curves of Au electrodes covered with the thiols under study in presence of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox system show pronounced differences which may be related to the structure of the organic molecules. Fig. 5, a to c compare the polarisation curves of pure Au electrodes and those covered with SAMs of the three thiols. The well pronounced peaks with a following plateau for the reactions of the redox system are included for comparison. The oxidation and reduction of the redox species is best suppressed by a modification with a TPMT film. No anodic or cathodic current peak is found and the plateau currents are not reached. Apparently, the large hydrated anions cannot penetrate the dense hydrophobic film of the SAM. Only a small residual current might pass along the TPMT molecules due to the interruption of the conjugated π -system. The TPT layer suppresses again the current peaks but the stationary current density is reached at ca. 0.8 V, i.e., 300 mV more positive. The largest currents are achieved for an AT film (Fig. 5, c). The anodic and cathodic

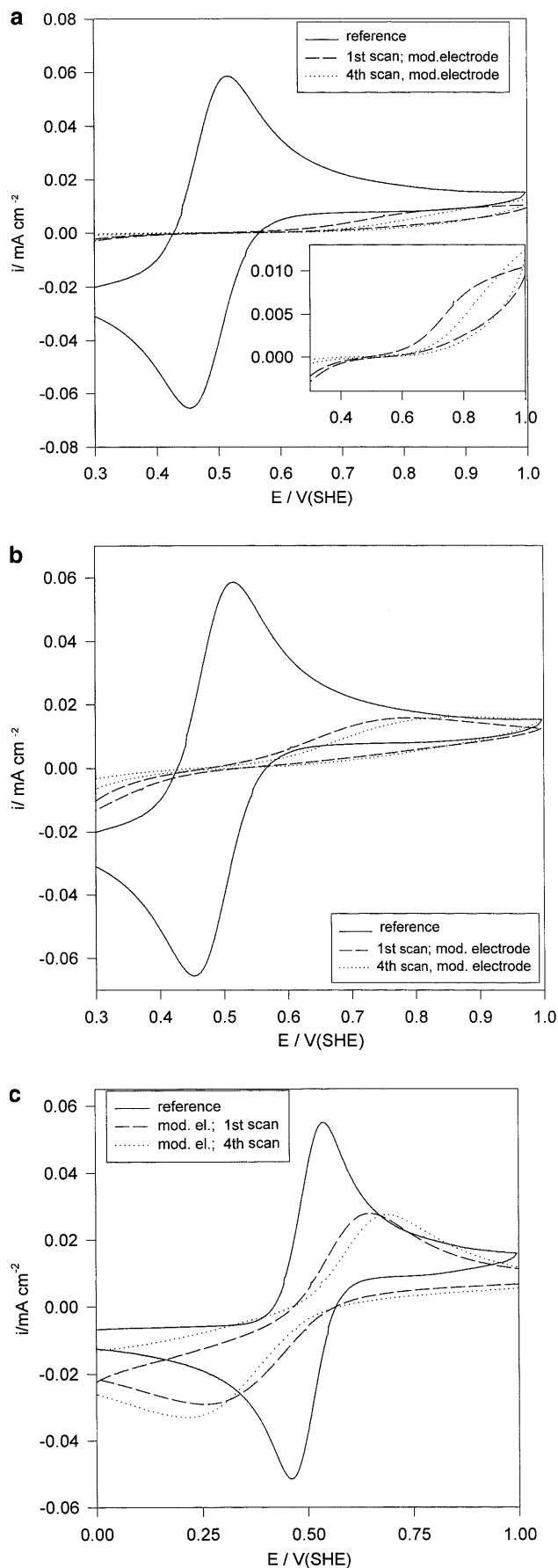


Fig. 5 Potentiodynamic polarisation curves of Au electrodes without (reference) and with inhibition by an SAM in 0.5 M $Na_2SO_4 + 0.005$ M $K_4Fe(CN)_6 + 0.005$ M $K_3Fe(CN)_6$, **a** 20 min exposure to 0.001 M TPMT, **b** 20 min exposure to 0.001 M TPT, **c** 60 min exposure to 0.001 M AT

peaks have about half the size of the reference and are shifted by 150 to 200 mV. Repetitive scans do not change the size and peak positions of the current-potential curves.

These simple electrochemical investigations of thiol-modified electrodes suggest the formation of a barrier type film for all three compounds within 20 to 60 min of exposure to a 10^{-3} M thiol solution. Apparently, these films are not destroyed during repetitive scans into the potential range of oxide formation. TPMT films also inhibit the oxidation and reduction of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox system. It appears that an effective electron transfer via the organic molecules of this layer is excluded although the three benzene rings are in conjugation, because the methylene spacer group between the aromatic system and the thiol group interrupts the electronic flow. This is not the case for the TPT layer with a possible electronic overlap of the π -electron system with the conduction band of the Au electrode. A small charge transfer is observed for the TPT-modified Au electrode, which joins the diffusion-controlled current density for large overvoltages. The largest current density is obtained for an AT-modified Au electrode although it is covered by a dense film which prevents effectively the anodic oxide formation. For this SAM a larger separation of the current peaks is observed with respect to the pure Au surface. However, the electronic conductivity is hindered by the AT-SAM only to a small extent which suggests an effective electron transfer to and via the thiols to the Au electrode. These results can be directly correlated with the molecular structures of the three aromatic thiols. AT with its extended and closed aromatic system exhibits the best conductivity. In

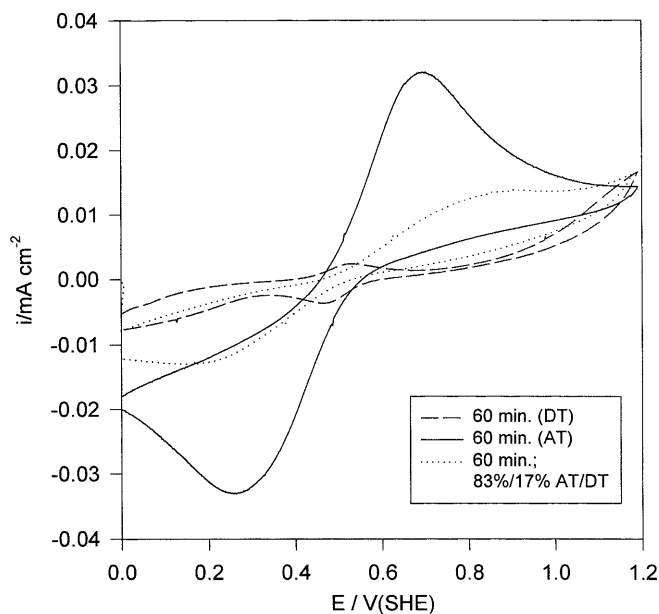


Fig. 6 Potentiodynamic polarisation curve of Au electrode, 10 mV/s with SAMs after 60 min exposure to DT, AT, and an 83/17 mixture of AT and DT

contrast, the aromatic system in TPT and TPMT is interconnected by σ bonds, leading to a less perfect overlap of π orbitals and thus to a lower conductance. In TPMT, this conductance is lowered further by the presence of the insulating methylene group. These observations suggest that a fine tuning of the barrier properties is easily possible by modification of the chemical structure of the constituents of the SAM.

An alternative path for the redox reactions, i.e., a transfer of the redox species via defects within the SAM to the Au surface may be ruled out. As has been shown clearly the oxide formation is seriously inhibited for all the examined thiols which indicates a negligible transfer of water molecules across the hydrophobic organic layer. Consequently, the organic molecules are densely packed with only a negligible fraction of the total defect area. However, the redox current may reach large values. Especially for the case of AT films it assumes 50% of that of an uncovered Au electrode. The transfer of hydrated redox species across the film or through defects should be even more difficult than that of water. Consequently, the prevention of oxide formation and large redox currents are an obvious sign for electronic conduction across the molecules.

Another way to tune the barrier properties of SAMs is the use of mixed monolayers. DT forms SAMs with a well developed barrier character. Fig. 6 shows the polarisation curves of a DT- and AT-modified surface in

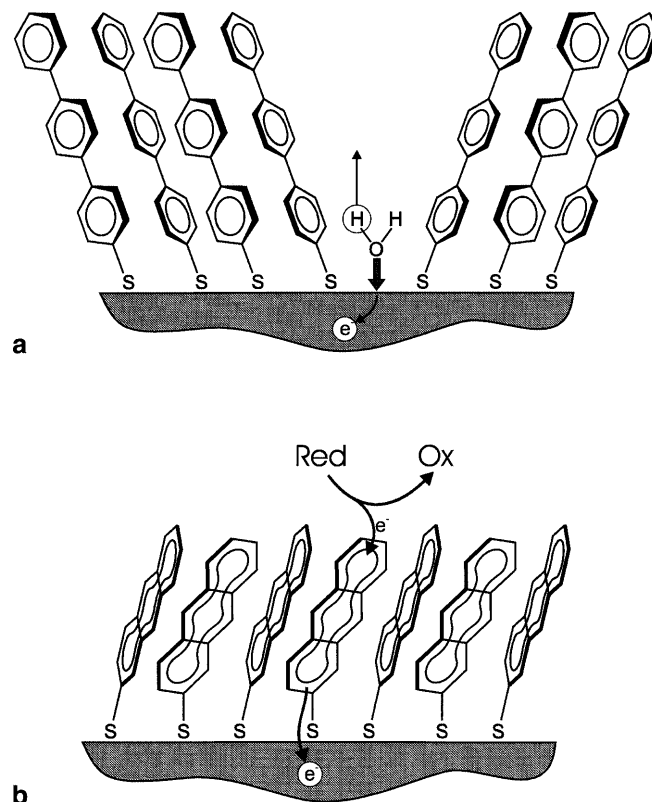


Fig. 7 Models for **a** oxide formation at defects, **b** electron transfer from a redox system via TPT-molecules to the Au-substrate

hexacyanoferrate solution. A 60 min exposure to the thiol solutions causes strong inhibition of the redox reaction in the DT solution with much smaller currents in comparison to an exposure to the AT solution. The exposure to a 83/17% mixture of both thiols yields a situation with anodic and cathodic currents of intermediate size. Whether this surface preparation forms domains of both thiols or a more homogeneous distribution or even a distribution on a molecular level should be examined with appropriate methods, e.g., STM. The present state of the experiments suggests interesting studies with a systematic variation of the electrode preparation to obtain surface regions with and without redox activity. This could even open a possibility for the study of electronic conduction via single molecules.

Conclusion

The three thiols examined form a continuous cover of an Au electrode with SAMs which prevent the access of water to the metal surface and thus oxide formation if the electrode is immersed sufficiently long in a 10^{-3} M solution (Fig. 7). Depending on the structure of the organic compounds one observes a charge-transfer reaction via the SAM or a suppression of the redox reaction. Alkanethiols show almost no redox reaction whereas mixtures of dodecanethiol with anthracenethiol afford an intermediate situation. These studies suggest the electron transfer via the molecules of the SAM film. Investigations with a large lateral resolution, i.e., by STM, should provide a more detailed insight into the

conduction mechanism, hopefully down to the molecular level.

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