INVESTIGATIONS ON THE OXIDATION AND REDUCTION OF FERROCENTHIOLS

N. Krings[1], H.-H. Strehblow[1], B. Zeysing[2], A. Terfort[2]

1) Heinrich-Heine University Duesseldorf, Universitaetsstr. 1, 40225 Duesseldorf

2) University Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg

Thiols have been studied extensively in recent years because of their ability to form self assembled monolayers (SAM) on noble and semi-noble metals opening an interesting field of research in nano-scale electrochemistry. Among the various available thiols ferrocenthiols attracted our interest because of the possibility to oxidize the ferrocen head group to ferrocenium and vice versa.

We investigated the electrochemical properties of SAMs of the ferrocenthiols shown in Fig. 1 on a Au(111) surface by cyclovoltammetry. The process of oxidation and reduction was followed by X-ray photoelectron spectroscopy (XPS). In addition the structure of the SAMs on Au have been examined with scanning tunnelling microscopy (STM).

Potentiodynamic polarization curves of the thiols were carried out in 0.001 M aqueous Na_2SO_4 solution (pH=7), phtalate buffer (pH=5.5) and 0.001 M perchloric acid (pH=3). They yield information on the oxidation- and reduction-potentials of the ferrocenthiols (Fig. 2). Additionally these curves allow the test of the quality of the SAM by potential increase to the range of Au-oxide formation and oxygen evolution. Fig. 2 compares the CV of a free and a thiol covered Au electrode with the apparent suppression of oxide formation of a SAM covered surface.

The oxidation and reduction of the ferrocenee head group was followed by XPS and the deconvolution of the $Fe2P_{3/2}$ signal into Fe(II) and Fe(III) contributions. The electrochemical preparation of the thiol covered Au surface under protection of purified Ar-atmosphere and its transfer to the UHV of the analyzer chamber within a closed system prevents any surface contamination and Fe(II) oxidation by oxygen. Fig. 3 depicts the decrease of the Fe(III)/Fe(II) ratio with the reduction time at E = -0.3 V. Apparently the necessary charge transfer during the reduction and oxidation of the head group occurs along the molecules to the Au surface.

STM investigations open a possibility to follow the structural arrangement of the thiol molecules within the SAM and its changes during the redox reaction of the head group. The oxidation state of the ferrocene unit determines the contact angle of water droplets. It usually gets smaller during oxidation but also the opposite is possible depending on structural changes with potential. Possible technical applications of the change in hydrophobicity of these SAMs with oxidation state will be discussed.
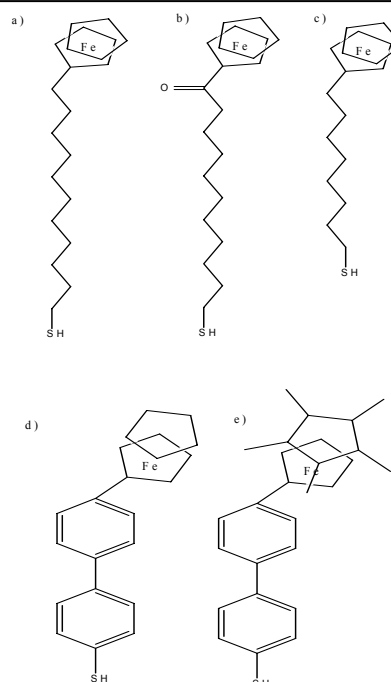

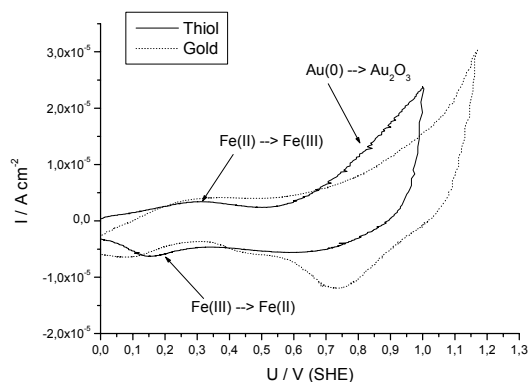Fig. 1: Thiols used for the experiments

Fig.2: Potentiodynamic polarization curves of an uncoated gold electrode and a thiol (Thiol e in Fig. 1) covered gold electrode.
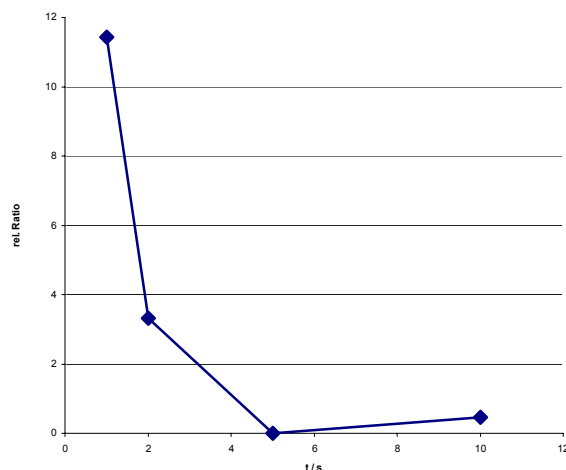

Fig. 3: Ratio of reduced and oxidized ferrocenthiol dependent on the time of reduction at -0.3 V (SHE) deduced of the Fe 2p3/2 XPS signal