

STABILITY AND APPLICATIONS OF ELECTROCHEMICALLY-ACTIVE SELF-ASSEMBLED MONOLAYERS

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0. Abstract

The electrochemical stability of monolayers is important for future applications. A potential window for self-assembled monolayers in aqueous inert electrolyte was obtained using Cyclic Voltammetry, Electrochemical Impedance Spectroscopy and Heterogeneous Electron Transfer. Also electrochemical techniques can be used for sensing applications. We investigated mixed monolayers of ferrocenethiol and an acid alkylthiol. Deprotonation of the acid by an alkaline electrolyte influences the other part of the mixed monolayer. The formal potential of ferrocene is shifted about 150 mV cathodically by the negative charge in the carboxylate part of the layer.

Keywords: monolayer, electrochemistry

1. The Electrochemical stability of self-assembled monolayers.

The use of self-assembled monolayers of sulfur containing adsorbates on gold in electrochemical applications requires monolayers that are electrochemically stable [1,2,3]. Therefore, monolayers of the five adsorbates in Figure 1 were prepared and investigated for their stability towards an electrical field. The adsorbates differ in type of attachment to the gold (thiol vs. sulfide) and number of attachments points (1-4). Two parameters were used to follow the change in quality of the monolayer: the resistance and the capability to block an external redox-couple (HET). Figures of the quality of the monolayer vs. the applied potential for the decylthiol **1** and cavitand **5** are depicted in figure 2. The gray window indicates the potential area where the decylthiol and cavitand monolayers are electrochemically stable. This windows ranges from -0.9 to +0.4 V_{MSE} . The decylthiol monolayer is a little bit more stable at the cathodic side of the window. Figure 3 shows the electrochemical stability for three differently benzene derivatives with two sulfide units for the attachment to gold. The quality of these three monolayers is of an order of magnitude lower than the decylthiol and cavitand monolayer (more current is going through the monolayer in the HET and the resistance of the monolayer is smaller). The potential

window for these monolayers is a little bit smaller: +0.4 to only -0.8 V_{MSE} . Furthermore there are no big differences in stability between the three differently substituted benzenes.

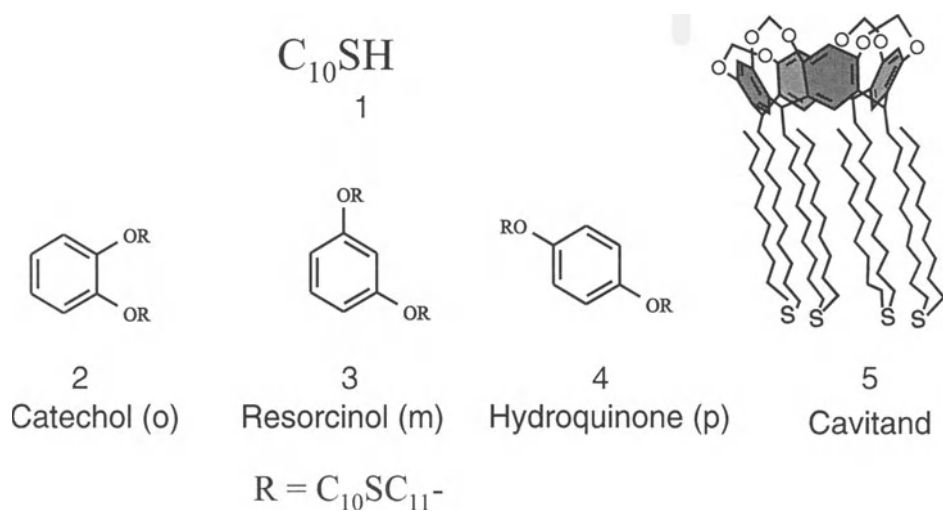


Figure 1. Adsorbates used for the electrochemical stability measurements.

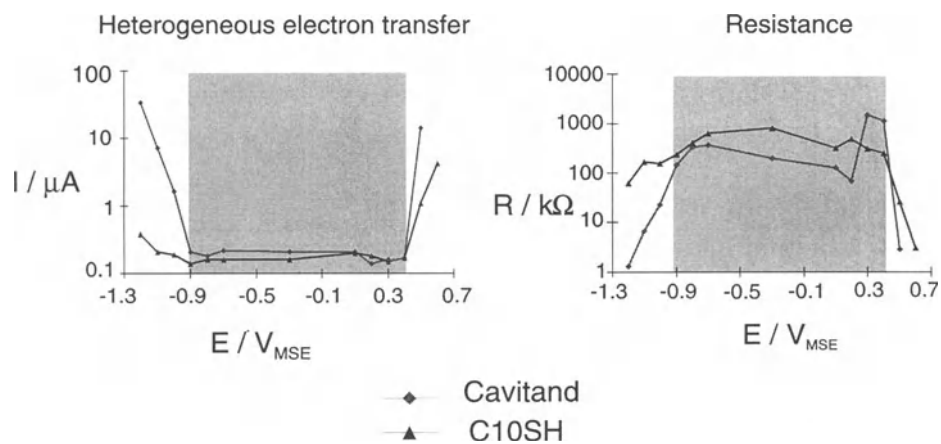


Figure 2. Potential window for decylthiol and cavitand monolayer.

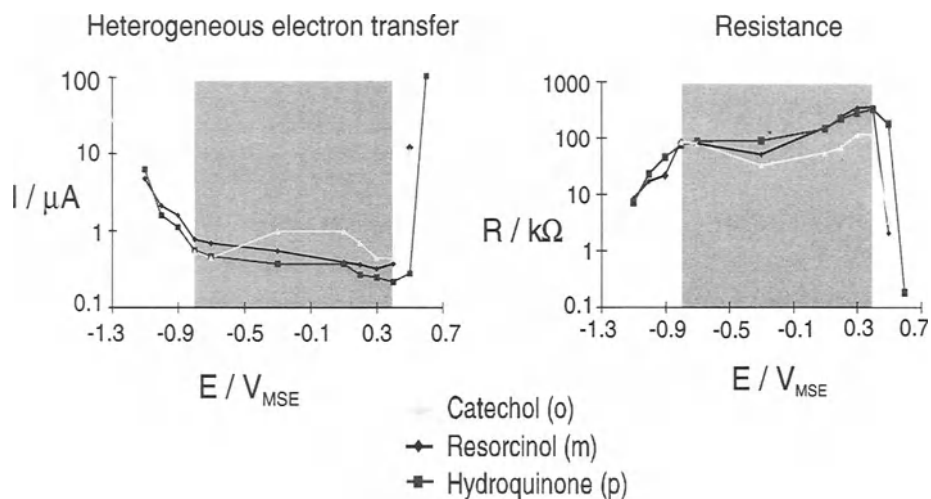


Figure 3. Potential window of differently substituted benzenes.

The potential window where self-assembled monolayers are electrochemically stable is thus from -0.8 to $+0.4$ V_{MSE} . The quality of the decylthiol and cavitand monolayer is higher than of the three substituted benzene derivatives.

2. pH-dependent response of mixed monolayers of ferrocene and acid.

Simple ferrocenethiol monolayers are electrochemically well-defined and easily prepared. Electrochemically-active self-assembled monolayers can be used for sensor-experiments in several ways. The receptor part can be present in the redox-molecule. A new approach uses mixed monolayers of an electrochemically-active adsorbate and a receptor adsorbate. Complexation at the receptor part of the monolayer causes a change in the surrounding of the redox-center and might lead to a shift in redox-potential. In this system there is a transfer of information from the receptor part to the other part of the mixed self-assembled monolayer, the redox center. Experiments were performed with a mixed monolayer of ferrocenethiol ($Fc-C_6-SH$) and an acid-thiol ($HOOC-C_7-SH$).

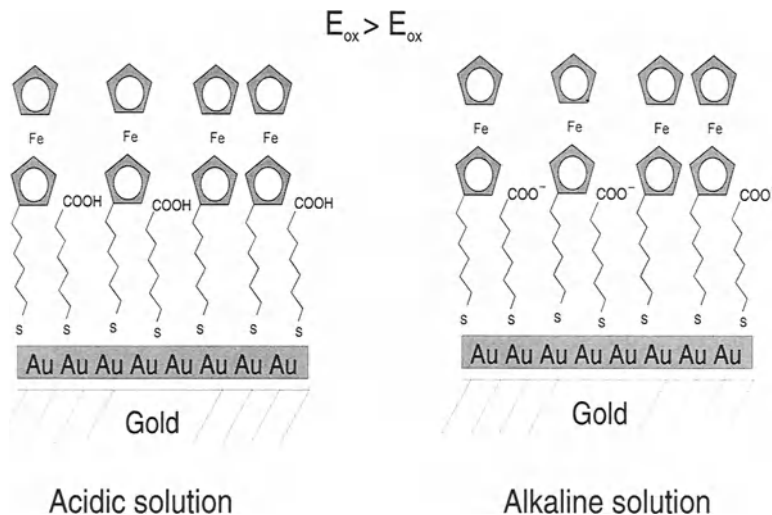


Figure 4. Mixed ferrocene/acid monolayer for sensor experiments.

Raising the pH of the electrolyte will deprotonate the acid function in the monolayer. The resulting negative charge can favor the ferrocene oxidation and shift it cathodically (oxidation at a lower potential). The mixed monolayer shows a clear pH-dependent response of the ferrocene (see Figure 5, mixed monolayer of 25% ferrocene and 75% acid in adsorbate solution). In HClO_4 (0.1M) the formal potential of the ferrocene has a value of $-130 \text{ mV}_{\text{MSE}}$ (see Figure 5). Changing the pH from 1 to 10 results in a broad peak at about $-130 \text{ mV}_{\text{MSE}}$ and an extra peak at about $-300 \text{ mV}_{\text{MSE}}$ is present. The shift of the redox peak (the deprotonation and protonation of the acid) is nearly reversible as changing the pH back and forward results in the same spectra. Information is transferred in a mixed self-assembled monolayer and measured electrochemically via the non-receptor part.

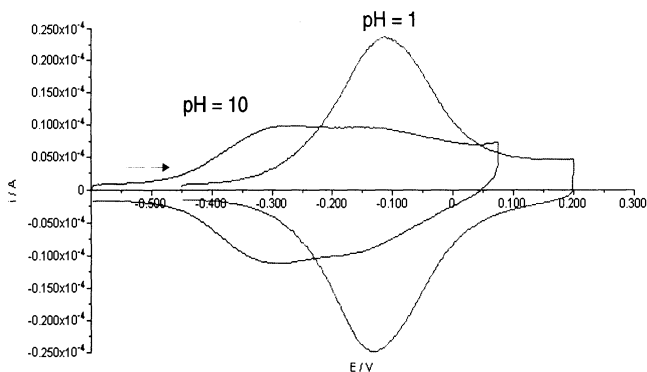


Figure 5. CV's of a mixed ferrocene/acidthiol monolayer at different pH's.

3. References

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