Graphical Abstract

Complementary electrochemical ICP-MS flow cell and in-situ AFM study of the anodic desorption of molecular adhesion promotors

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Highlights

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- Anodic corrosion protection of SAMs on Au with varying hydrophobicity are compared.
- Intermolecular forces control the behaviour of SAMs during anodic polarization
- Hydrophobic SAM enhances corrosion resistance via micelle formation at interface.
- Hydrophilic SAM remains weakly surface bound as a highly mobile layer.
Complementary electrochemical ICP-MS flow cell and in-situ AFM study of the anodic desorption of molecular adhesion promotors

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Abstract

Molecular adhesion promoters are a central component of modern coating systems for the corrosion protection of structural materials. They are interface active and form ultrathin corrosion inhibiting and adhesion-promoting layers. Here we utilize thiol-based self-assembled monolayers (SAMs) as model system for demonstrating a comprehensive combinatorial approach to understand molecular level corrosion protection mechanisms under anodic polarization. Specifically, we compare hydrophilic 11-Mercapto-1-undecanol and hydrophobic 1-Undecanethiol SAMs and their gold-dissolution inhibiting properties. We can show that the intermolecular forces (hydrophobic vs hydrophilic effects) control how SAM layers perform under oxidative conditions. Specifically, using \textit{in situ} electrochemical AFM and a scanning-flow cell coupled to an ICP-MS a complementary view on both corrosion resistance, as well as on changes in surface morphology/adhesion of the SAM is possible. Protection from oxidative dissolution is higher with hydrophobic SAMs, which detach under micelle formation, while the hydrophilic SAM exhibits lower protective effects on gold dissolution rates, although it stays intact as highly mobile layer under anodic polarization. The developed multi-technique approach will prove useful for studying the interfacial activity and corrosion suppression mechanism of inhibiting molecules on other metals and alloys.

\textbf{Keywords:} corrosion protection, electrochemical AFM, self assembled monolayers, electrochemical ICP-MS, molecular adhesion promotors

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1. Introduction

Organic coatings are widely used as corrosion protecting layers on metals. Coatings protect from corrosion by a physical barrier effect for water between the metal and its surrounding, and are therefore up to a few micrometer in thickness. Still, the most crucial part of the coating is at the boundary of the organic top coating with the metal (oxide) underneath. Additionally, molecules such as silanes, or phosphonates which can form self assembling molecular thin films/monolayers (SAM) at an interface, are typical reactive additives for coating formulations. Specifically, SAMs have been proven to be suitable as molecular adhesion promotors for long-term corrosion protection. Further, the covalent character of the head group to metal(oxide) bond stabilizes as a linking layer between the metal(oxide) and the further covalent attachment of polymer layers on metallic substrates.

In particular, the system of gold and thiol-based self-assembled monolayers (SAMs) is well studied as model system due to its ease of preparation, and stability and quality of the layers. For thiol-based SAMs the bond strength between the sulfur of the thiol and the gold determines the stability of the formed monolayer. e.g. iodide can result in delamination of the formed SAM. Potential dependent SAM formation has been measured ex situ with Scanning tunneling microscopy (STM), but not yet under operating conditions at oxidative/anodic potentials. Further, weakening of the bond for removal of the formed SAM by cathodic desorption (stripping) is a well established process.

The oxidative desorption on the contrary is less studied. Though electrochemical anodic detachment already finds application in formation of mixed SAM layers by partial electrochemically induced desorption of a SAM in a thiol solution. Further, polarization of the surface can enhance the adsorption kinetics of molecular thin films. How molecular adhesion promotors act, and to which degree they suppress metal dissolution, when the underlying substrate is electrochemically polarized into anodic polarization is still unclear.

In recent years, elementally resolved electrochemical techniques such as combinations of flow cells with downstream inductively coupled plasma mass spectrometry (ICP-MS) or optical emission spectrometry (ICP-OES) analysis, proved to be useful for understanding molecular dissolution mechanisms at electroactive interfaces. These techniques have been applied to study the dissolution of Zn coatings on steel, the dissolution of
electrocatalysts under operating conditions, or to the study of the potential dependent stability of photo-electrocatalytic materials. Here, we extend this technique to understand corrosion inhibiting effects of molecular adhesion promotors under anodic polarization, as a model system for more complex alloys and inhibitors.

Specifically, we report results on the in situ anodic polarization of SAM covered gold in sodium perchlorate solution. We compare Linear Sweep Voltammetry in hand with in situ electrochemical topography scanning with an atomic force microscope (EC-AFM) and elementally resolved ICP-MS dissolution currents of hydrophobic and hydrophilic SAMs. We demonstrated a significant corrosion-inhibiting effect of SAMs at anodic potentials, and show how interfacial hydrophobic forces can result in a micelle formation at the interface. This comprehensive approach combines complementary interface sensitive techniques for providing a detailed insight into molecular level protection mechanisms of molecular adhesion promotors during anodic polarization.

2. Experimental Section

**Chemicals and Sample preparation**

Electrolyte solutions were prepared from NaClO₄ (98%, Alfa Aesar) and Milli-Q water (resistivity >18 MΩ·cm, total organic carbon < 4 ppb). 11-Mercapto-1-undecanol (97%, Sigma Aldrich), 1-Undecanethiol (98%, Sigma Aldrich) were diluted to 1 mM solutions in Ethanol (chromatography grade, Carl Roth) for coating of the substrates. Molecularly smooth gold surfaces of 70-100 nm thickness were prepared by template stripping from mica using an established protocol. Samples are contacted with 0.125 mm diameter gold wire (99.99%, Goodfellow Cambridge Ltd.), and immersed for min. 12 h in ethanolic SAM solution. To remove excess thiols surfaces are rinsed thoroughly with ethanol, hexane and ethanol and dried with a gentle N₂ stream. The surface wettability of the formed SAMs is confirmed by contact angle measurements shown in the Supporting Information (SI) Fig. S1

**Atomic Force Microscopy**

AFM topographies were taken with a Cypher ES (Asylum Research, Oxford Instruments, Santa Barbara, US) using Arrow™ UHFAuD (NanoWorld, CH) and SCOUT 350 RAu (NuNano, GB) probes. Photothermal excitation
is used with amplitude modulation (blueDrive) as driving mode. The electrochemical cell is a home-built modification with a platinum foil as a counter electrode and the reference electrode being connected via a capillary to the enclosed cell. $\text{NaClO}_4$ with a concentration of 10 mM is used.

**Inductively Coupled Plasma Mass Spectrometry**

Measurements were carried out with an Agilent 7900 ICP-MS (Agilent Technologies, US), a collision cell with 5 mL/min flow of helium as cell gas was used. Calibration was performed with multi-element standard (Inorganic Ventures, US). For ICP-MS, downstream of the electrochemical cell, the analyte was mixed with internal standard solution, containing Cobalt an Thallium. Electrochemical experiments were conducted in a home-built flow cell out of PEEK and PTFE. The exposed electrode area is circular and sealed with a 3 mm inner diameter O-ring. Before each experiment the electrolyte (100 mM $\text{NaClO}_4$) was purged with compressed and filtered air for at least 30 minutes to guarantee the same concentration of dissolved oxygen.

**Electrochemistry**

A Biologic VSP-300 potentiostat (Biologic, France) or a PalmSens 4 (PalmSens BV, NL) were used for electrochemical measurements. All electrochemical experiments were performed with a Ag|AgCl-Electrode (Multichannel Systems, DE) as reference electrode. All presented data is referenced to that potential. Platinum is forming the counter electrode. Freshly prepared SAMs on gold get - after a short equilibrating time in the electrolyte (10 mM $\text{NaClO}_4$ for AFM, 100 mM for ICP-MS) - polarized from 0.0 to 1.5 V vs. Ag|AgCl with a scan rate of 5 mV/s. Higher scan rates tested showed no notable difference.

3. Results and Discussion

In this work we experimentally characterized the corrosion inhibition properties of hydrophilic and hydrophobic self-assembled monolayers (SAMs) on gold under potential control. As shown in Fig. 1, we selected a hydrophobic and a hydrophilic tail group termination, in order to study the effect of the wettability of the substrate.

Therefore, the used SAMs are characterized by their same length of the hydrocarbon chain, but a major difference in interaction with water due to the selected tail group. 11-**Mercapto-1-undecanol** ($\text{OH}$-SAM) with its
hydroxyl-terminated tail is hydrophilic, whereas \textit{1-Undecanethiol} (\(CH_3\)-SAM) creates a hydrophobic layer on the gold. As Fig. 2 A & B show, the preparation produced - as expected from literature - an uniform and smooth film with typical defect patterns at domain boundaries of the formed SAMs.

These SAMs were consequently anodically polarized in \(NaClO_4\) solution to 1.5 V in order to characterize their corrosion inhibiting behaviour during anodic polarization using Linear Sweep Voltammetry (LSV). The electrolyte was chosen for its widespread application in electrochemistry. The data was further complemented by \textit{in situ} and \textit{ex situ} AFM topography scanning, as well as by online ICP-MS flow cell analysis of the anodically dissolving gold. The results of these analyses can be summarized as follows:

First, \textit{ex situ} topographies (Fig. 2) compare the initial conditions of the surfaces modified with the respective SAMs (indicated by subscript 1) with a topography after polarization. For the hydrophobic \(CH_3\)-SAM the surface after polarization (A2) shows two topographic features, which are (1) globular residues likely formed by disintegrated SAM, as well as (2) nano-scaled grains as expected for a neat template stripped gold surface. This behaviour suggests that the \(CH_3\)-SAM disintegrates completely during anodic oxidation, meaning that a disordering of the assembled structure is accompanied with lower molecular coverage due to partial SAM dissolution. In contrast, the hydrophilic SAM still shows similar structures before and after polarization, indicating an almost unaltered and likely intact SAM.

Hence, the tail group directly determined how the SAM behaves during polarization. It appears likely, that the thiol|gold bond is weakened by the growth of an underlying oxide film, which in turn can cause a disintegration of the hydrophobic SAM. This disintegration can be driven by the tail group effect as follows: Weakening of the surface bond can trigger the formation of bilayer structures, or can even drive micelle/particle formation as observed for weak binding of phosphonate SAMs on alumina, if the hydrophobic
Figure 2: *Ex situ* AFM topographies of self assembled monolayers on gold before (1) and after (2) polarization to 1.5 V for $CH_3^-$ (A) and $OH^-$ (B) SAMs.
interaction of the tail groups overpowers the thiol|gold binding. In contrast, if the SAM molecules are terminated by hydrophilic tail groups there is no direct driving force for a disintegration of the SAM, and the intramolecular hydrophobic interactions within the SAM can withstand the "rolling up"/lift-off of the SAM. As such, for the OH-SAM, the weakening of the thiol bond may result in a "flying carpet like" situation during anodic polarization, with a detachment of the SAM and interim re-attachment.

To further support this interpretation, we performed in situ AFM under potential control. Fig. 3 shows an image of the representative scan, when a significant change of the surface topography was observed during anodic polarization. Videos of the entire topographic evolution during polarization are available for download as SI.

In detail, the hydrophobic SAM (Fig. 3 A) is showing a roughening of the surface starting at 0.75 V, in terms of formation of particulate residues (marked by arrows in figure). This is consistent with the interpretation of a weakening of the thiol|gold bond and a consequent triggering of a SAM lift-off due to formation of micellar structures, which is driven by the hydrophobicity of the molecules, as it is known for the stabilisation of gold nanoparticles. The roughening of the CH₃-SAM hence indicates an initial detachment of the thiols accompanied by micelle formation. In contrast, the hydrophilic SAM appears intact up to more than 1.2 V where we see considerable flattening.
of the surface. This flattening is indicative of a lift-off of the SAM as a "flying carpet", i.e. the thiol-gold bond is weakening, and as a result a more mobile, less defect rich SAM structure forms, and does also not impregnate the underlying granular structure of the gold. The templating of the surface roughness of the gold into the SAM surface is less pronounced. As seen in the \textit{ex situ} data (see again Fig. 2 B2) the SAM remains then intact and reforms after polarization, without lifting off from the surface. (Contact angles \textit{cf. SI Fig. S1} also stay similar after polarisation.) The mechanism of the reformation of the gold-thiol bond remains unclear. Future work might track the changes on the interface by means of XPS, as it has been already shown for the influence of halides on SAMs in our former work. \textsuperscript{[8]}

Based on the nanoscopic understanding of the SAM behaviour during polarization we performed additional \textit{in situ} spectroelectrochemical analysis, \textsuperscript{[20]} \textsuperscript{[19]} \textsuperscript{[17]} to understand how these SAM structures inhibit or enhance gold dissolution during oxidative polarization.

\textbf{Fig. 4} shows (a) the measured current during electrochemical polarization as well as (b) the elementally resolved dissolution current of the gold dissolution (ICP-MS) displayed as a function of the linearly increasing potential. For both, data of more than 8 independent measurements are compiled for each SAM sample (OH and CH$_3$) and are further compared to the data obtained for bare gold. For the elemental dissolution current (ICP-MS) shown in panel B the observed range (shaded areas) as well as the mean dissolution current are displayed (solid lines). For the current, two examples are shown, as less variation is observed.

The electrochemical current shown in panel A and as marked indicates the initial gold oxidation at the expected potential, as well as the increasing current at higher polarizations due to water splitting. Statistically, there is no large difference in the absolute observed currents. (Linear Sweep Voltammograms under stagnant conditions are in the SI Fig. S2)

However, the ICP-MS dissolution currents of gold exhibit clear changes, and an inhibition of the anodic dissolution of gold for the CH$_3$-SAM and the OH-SAM (shown in Fig. 4 B) compared to unmodified gold is obvious. In detail, both SAMs statistically shift the onset of rapid gold dissolution to higher potentials. At a threshold dissolution rate of 0.01 ng/cm$^2$/mV the onset of dissolution for the OH-SAM is slightly shifted to 1.00 V compared to pure gold (0.98 V), the CH$_3$-SAM shows a shift to 1.13 V. It is worth noting that the recorded dissolution rates show a significant variation although preparation remains the same, indicating an influence of defects formed during
Figure 4: Linear Sweep Voltammetry (LSV) of bare gold (black), gold covered with a hydrophilic (red) and hydrophobic (green) self-assembled monolayer. Shaded areas indicate the range of observed dissolution profiles over at least nine experiments. A) Electrochemical Polarization Curves. B) Dissolved gold during LSV. Solid lines represent the average curves over all of one type. Dashed lines and circles indicate a onset dissolution rate of 0.01 ng/cm²/mV. Inset shows total integrated dissolved mass of gold during LSV, whiskers indicate the confidence interval (CI) of 95%.
SAM formation. Nonetheless, statistical trends hold over a large set of >8 experiments for each sample.

All of the curves have in common a two-step dissolution profile with a small shoulder of comparatively little dissolution starting with the gold oxidation, followed by a steep increase in amount of gold released to solution during water splitting. Previous work by Cherevko et al. [20] traced this behaviour back to initial small dissolution from formation of gold oxide and later on more drastic degradation during water splitting, which is consistent with our data of SAM coated substrates.

The inset in Fig. 4 B shows the integrated amount of dissolved gold, further confirming this trend. Dissolution for all of the systems tested correspond to only a fraction of a single layer of gold which would result in a total of ≈ 450 ng/cm² gold dissolution. As expected the uncoated gold shows the highest dissolved mass, OH- as well as CH₃-SAM modified gold show a decreasing trend to about 30% lower overall gold dissolution. The SAM coating can hence significantly suppress gold dissolution, likely by a barrier effect, and potentially also by stabilisation of the surface atoms at the SAM oxide interface.

Surprisingly, the least gold is released from the CH₃-coated surface, although the SAM lift-off is observed at the lowest potentials in AFM and the SAM indicates a significant roughening. The shoulder of the gold oxidation, while clearly visible in the electrochemical data in Fig. 4 A, is less pronounced in the dissolution rates for the CH₃-SAM. This indicates that the hydrophobic SAM incorporates (otherwise dissolving) Au atoms into a surface bound micellar structure.

Further, looking at the ranges of dissolution recorded (indicated by the shaded areas) the hydrophobic SAM (green) clearly shows an onset of gold dissolution at higher potentials compared to hydrophilized and bare gold. Bare gold and OH coated gold overlap over most of the potentials, just for very high potentials at above 1.4 V gold with OH-SAM seems to be slightly less dissolving. The average dissolution curve for the CH₃-SAM rises later and for the whole potential range stays well below the dissolution rates of the other systems tested. As such, and in agreement with our interpretation, the hydrophobic CH₃-SAM may form micelles, which may lead to a trapping of gold within micelles, hence lowering the total dissolved ion count initially. This initial low count is followed by the steepest rise of the dissolution, at higher potentials, where trapped micelles may desorb.

This is an interesting behaviour, which we can interpret as a potentially
important fundamental step during technical processes such as interphase formation during polymer coating (gluing/ coating for corrosion protection, etc.) of a metal in an oxidative environment. Interphases are considered boundary layers of a metal|polymer interphase where it has been speculated that metal ions dissolve and stabilize into the polymer matrix due to their interaction with the functional groups of the polymer. Our data demonstrates that such a metal dissolution mechanism is possible, and appears to be favoured by intermolecular interactions that drive micelle formation, or in other words the enclosure of metal ions in an functional organic matrix that is in contact with the metal during oxidation.

4. Conclusions

We successfully compared AFM imaging and ICP-MS flow cell studies of the anodic detachment of a protective thin film on gold. We demonstrated their corrosion-inhibiting effect at anodic potentials. The morphological changes of two SAMs (11-Mercapto-1-undecanol and 11-Undecanethiol) on gold during anodic polarization show a strong effect of the tail group in in situ AFM. Quantification of the dissolved gold with a scanning-flow cell coupled to an ICP-MS certainly adds information gain to the pure electrochemical data and might prove useful for the study of further coatings on metals, also in more corrosive electrolytes as halides.

Our results suggest the following specific conclusions:

- Hydrophobic molecules may immobilize dissolving metal ions in micelles, which may enclose metallic (or oxidic) nanoparticles formed during anodic oxidation.

- During this process the SAM disintegrates and dewetting from the oxidized gold interface occurs.

- This data may show initial fundamental steps which occur during interphase formation when a coating or glue is applied to a metallic substrate.

- Hydrophilic molecules tend to not detach, but form a weakly adhering and highly mobile layer without significant micelle formation. This results in lower initial retardation of metal dissolution.
This combinatorial multi-technique approach will prove useful for studying the interfacial activity and corrosion suppression mechanism of inhibiting molecules on other metals and alloys.

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Competing Interests

The Authors declare no Competing Financial or Non-Financial Interests.

Data availability

The raw and processed data required to reproduce these findings are available from the corresponding author via www.repositum.tuwien.ac.at upon reasonable request.

Author Contributions

Dominik Dworschak: Investigation, Methodology, Visualization, Writing-Original Draft, Writing-Reviewing and Editing. Carina Brunnhofer: Investigation, Data Curation. Markus Valtiner: Conceptualisation, Writing-Reviewing and Editing, Funding acquisition, Supervision.

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SUPPORTING INFORMATION

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Figure S1: Contact angles of gold and SAM coated gold surfaces. Contact angles did not significantly change after treatment with LSV in NaClO₄
Figure S2: Linear Sweep Voltammetry of SAM covered Au with OH (red) and $CH_3$ functionality. Gold and SAM oxidation cannot be distinguished from each other.