

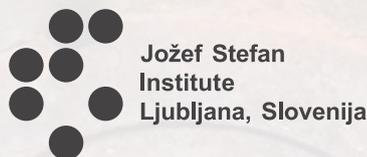
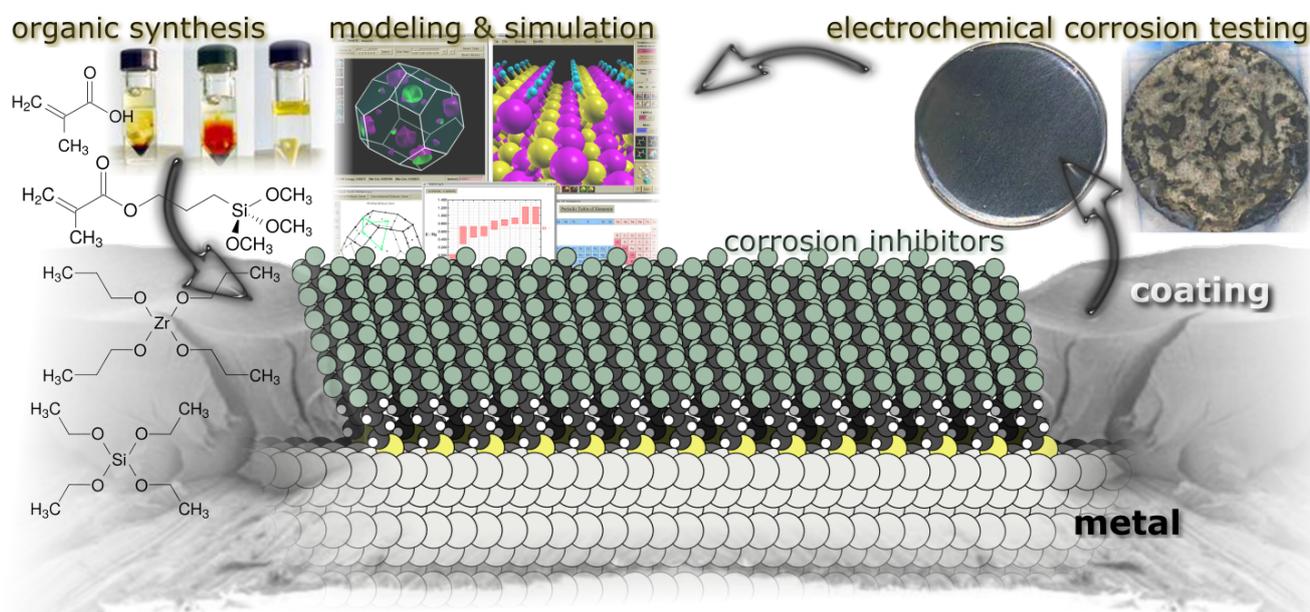
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29	30	13
Cu	Zn	Al
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June 11–13, 2018  
Ljubljana, Slovenia

Workshop on  
integrative approaches  
to corrosion research

# Book of Abstracts



Jožef Stefan  
Institute  
Ljubljana, Slovenija



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## Sponsors

**CorrTalk** 2018 is a workshop organized in the context of the following two M-era.Net sponsored projects: “**COR\_ID – Design of corrosion resistant coatings targeted for versatile applications**” ([http://cor\\_id.ijs.si/](http://cor_id.ijs.si/)) and “**COIN DESC – Corrosion inhibition and dealloying descriptors**” (<http://coindesc.ijs.si/>).

The **COR\_ID** project consortium comprises researchers from three partner countries: Slovenia, France, and Hungary. The **COIN DESC** project comprises researchers from four partner countries: Slovenia, Belgium, Spain/Catalonia, and the Netherlands.

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- Netherlands: Netherlands Organisation for Scientific Research

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## Organizers

**Ingrid Milošev** (*Jožef Stefan Institute*)

**Anton Kokalj** (*Jožef Stefan Institute*)

**Dejan Lorber** (*Talum d.d.*)

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**Matic Lozinšek** (*workshop programme scheduling*),

**Barbara Kapun** (*administration*)

*and all others who contributed.*

## Invited Speakers

**Rob Lindsay** (*The University of Manchester*)

**Philippe Marcus** (*CNRS - Chimie ParisTech*)

**Dominique Costa** (*CNRS - Chimie ParisTech*)

**Anikó Nemes** (*ELTE - Eötvös Loránd University*)

**Frank Uwe Renner** (*Hasselt University*)

**Daniel Crespo** (*Universitat Politècnica de Catalunya*)

**Arjan Mol** (*Technical University Delft*)

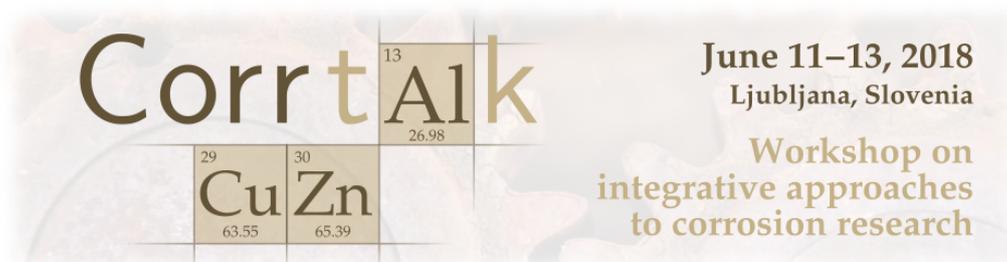
**Janez Kovač** (*Jožef Stefan Institute*)

## Scope of the workshop

**CorrTalk** 2018 is a workshop focusing on different approaches to corrosion research. The workshop aims to bring together scientists from a variety of fields such as electrochemistry, surface analysis and computational modeling in order to bridge the gaps between the fields and to obtain a better understanding of corrosion and corrosion inhibition.

## Where & When?

**CorrTalk** takes place at the Jožef Stefan Institute (Ljubljana, Slovenia) and in Talum d.d. (Kidričevo, Slovenia) from 11 to 13 June, 2018.



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## Monday, June 11

Color code: 30 min presentation 20 min presentation

## Program

9:00 – 9:10	Opening remarks	
9:10 – 9:40	<b>Rob Lindsay</b> (invited) <i>Insight into corrosion inhibition in acidic solutions</i>	
9:40 – 10:10	<b>Ingrid Milošev</b> <i>COR_ID: Design of corrosion resistant coatings targeted for versatile applications</i>	
10:10 – 10:30	Coffee break	
10:30 – 11:00	<b>Arjan Mol</b> (invited) <i>Local electrochemical and surface analytical analysis of corrosion and Cr(VI)-free protection of AA2024-T3</i>	
11:00 – 11:30	<b>Anton Kokalj</b> <i>Molecular modeling of corrosion inhibitors and a search for physically sound corrosion inhibition descriptors</i>	
11:30 – 11:50	<b>Urša Tiringler</b> <i>Hybrid sol-gel coatings for corrosion protection of aluminum alloys</i>	
11:50 – 12:10	<b>Shova Neupane</b> <i>AFM characterization and force measurements on inhibitor-modified Cu and Cu-Zn surfaces</i>	
12:10 – 14:00	Lunch break	
14:00 – 14:30	<b>Daniel Crespo</b> (invited) <i>Metallic glasses properties and corrosion performance</i>	
14:30 – 14:50	<b>Dunja Gustinčič</b> <i>New insights into adsorption bonding of imidazole on surfaces of metals</i>	
14:50 – 15:10	<b>Bálint Menczinger</b> <i>Preparation of (perfluoroalkyl)alkane thioacetates and their use in organic synthesis and corrosion research</i>	
15:10 – 15:30	<b>Fatah Chiter</b> <i>DFT modeling of the protection of aluminum by carboxylates against adsorption and diffusion of chloride</i>	
15:30 – 15:50	Coffee break	
15:50 – 16:20	<b>Dominique Costa</b> (invited) <i>DFT modeling of passive films on Al and AlCu alloys, role of defects and corrosion inhibition</i>	
16:20 – 16:40	<b>Pere Bruna</b> <i>AFM and potentiodynamic analysis of melt-spun Cu(Zn,Zr) under corrosion agents</i>	
16:40 – 17:00	<b>Marion van Midden</b> and <b>Matic Lozinšek</b> <i>Scrutinizing the bonding of 2-mercaptobenzimidazole on Cu(111) by STM and DFT</i>	
17:00 – 17:20	<b>Sandrine Zanna</b> <i>XPS analysis of aluminium samples exposed to organic molecules and saline water</i>	

## Tuesday, June 12

9:00 – 9:30	<b>Philippe Marcus</b> ( <i>invited</i> ) <i>A new experimental platform for surface science and corrosion studies</i>	
9:30 – 10:00	<b>Dejan Lorber</b> ( <i>invited</i> ) <i>title to be announced</i>	
10:00 – 10:20	<i>Coffee break</i>	
10:20 – 10:50	<b>Janez Kovač</b> ( <i>invited</i> ) <i>Application of surface analytical techniques XPS, SIMS and AES for corrosion studies</i>	
10:50 – 11:20	<b>Anikó Nemes</b> ( <i>invited</i> ) <i>Fluorous chemistry and fluorous surface modification</i>	
11:20 – 11:40	<b>Peter Rodič</b> <i>Superhydrophobic coatings on aluminium based on alkyl and fluoroalkyl silanes</i>	
11:40 – 12:00	<i>Coffee break</i>	
12:00 – 12:30	<b>Frank Uwe Renner</b> ( <i>invited</i> ) <i>Effect of inhibitor modifications on dealloying studied on the atomic scale: a surface science approach</i>	
12:30 – 13:00	<b>Matic Poberžnik</b> <i>Bonding of several corrosion inhibitors to oxidized aluminum surfaces</i>	
13:00 – 13:30	<i>Break</i>	
13:30 – 15:30	<b>Departure for <u>Talum</u> factory near <u>Ptuj</u></b>  (a light meal with doughnut will be provided at <u>Trojane</u>  )	
15:30 – 16:00	<b>Presentation of <u>Talum</u></b>	
16:30 – 18:00	<b>A tour of the <u>Talum</u> factory</b>	
18:00 – 20:00	Arrival at hotel <u>Mitra</u> (in the city of Ptuj)	
20:00 ...	<b>Workshop dinner</b> in restaurant <u>Ribič</u>	
After dinner	Wine tasting in hotel <u>Mitra</u>	

## Wednesday, June 13

9:00 – 11:30	Excursion and sightseeing in <u>Ptuj</u> (oldest recorded town in Slovenia)
11:30	Departure from Ptuj
13:00	<b>Arrival at Ljubljana airport</b>
13:45	Arrival in Ljubljana

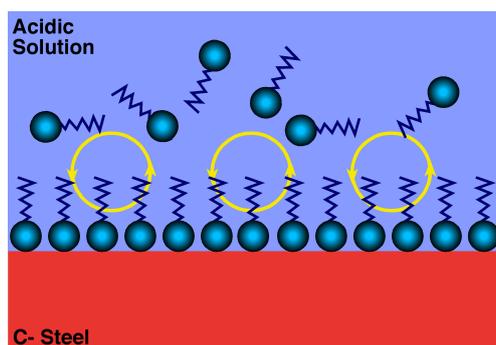
## **Abstracts – Monday 11 June**

## Insight into corrosion inhibition in acidic solutions

Rob Lindsay\*

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For more than a century, surface-active organic species have been employed to inhibit the corrosion of metals/alloys. Given suitable selection, such corrosion inhibitors have proven to be highly effective, preventing significant degradation of metallic substrates even in highly aggressive environments. Nevertheless, there are still considerable gaps in fundamental knowledge of corrosion inhibitor functionality, severely restricting rational development. For example, corrosion inhibition in acidic solutions is widely reported to be the result of the adsorption of a monolayer of surface-actives, as shown in Fig. 1. This description, however, can be considered to be largely a cartoon, as there is a lack of supporting experimental evidence. Many key details remain uncertain, including the surface chemistry of the inhibited substrate, the structure of the adsorbed CI layer and even its surface coverage. In this presentation, I will discuss efforts to address some of these issues through detailed interface characterisation to facilitate improved mechanistic understanding of corrosion inhibitor functionality. For example, I will present recent work demonstrating that surface adsorption is not always sufficient for achieving a target corrosion inhibition efficiency, i.e. it will be demonstrated that a surface-active can be bound to the surface, but not lead to sufficient reduction in corrosion rate. Moreover, I will outline our methodology for acquiring X-ray photoelectron spectroscopy (XPS) data from such interfaces, without the substrate undergoing significant post immersion oxidation.



**Figure 1.** Widely accepted modus operandi of organic CI species in acidic solutions.

## COR\_ID: Design of corrosion resistant coatings targeted for versatile applications

Ingrid Milošev,<sup>\*,1</sup> Dolores Zimerl,<sup>1</sup> Peter Rodič,<sup>1</sup> Tina Bakarič,<sup>1</sup> Barbara Kapun,<sup>1</sup> Pauline Cornette,<sup>2</sup> Sandrine Zanna,<sup>2</sup> Antoine Seyeux,<sup>2</sup> Stojan Stavber,<sup>1</sup> Anicó Nemes,<sup>3</sup> Bálint Menczinger,<sup>3</sup> Vanja Tubin,<sup>4</sup> Matic Poberžnik,<sup>1</sup> Dominique Costa,<sup>3</sup> Dejan Lorber,<sup>4</sup> Anton Kokalj,<sup>1</sup> József Rábai,<sup>3</sup> Philippe Marcus<sup>2</sup>

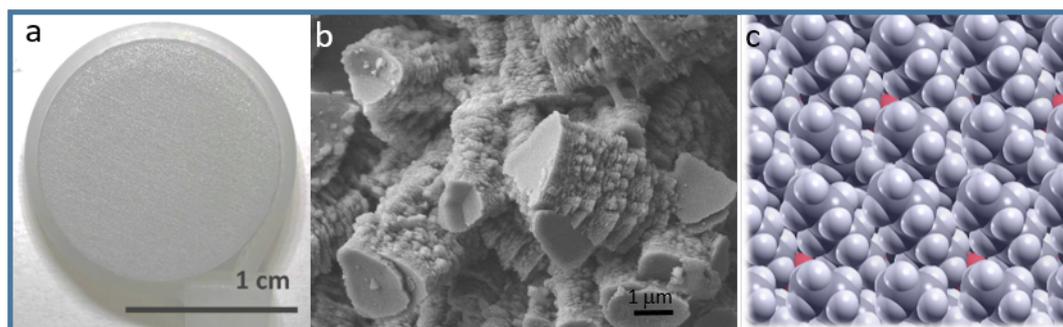
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The principle objective of the project COR\_ID is to design and engineer new coating materials with targeted properties of increased corrosion resistance, prolonged service life-time and reduced ecological impact. The project consortium links scientists from three partner countries and one technological company aiming to stimulate advances in basic and applied research and technology transfer. Multifunctional coatings would simultaneously act as high-quality corrosion inhibitors and offer additional properties like hydrophobicity. These coatings will be used also for less corrosion resistant Al alloys or secondary Al alloys by industrial partner Talum to improve the functional performance of some of their products. The project goals are being realized through the ICME (Integrated Computational Materials Engineering) paradigm consisting of integration of three fundamental disciplines: multi-scale modeling, multi-scale chemical synthesis, and high-throughput electrochemical and corrosion experimental testing and verification.



**Figure 1.** Macroscopic (a) and microscopic (b) image of etched aluminium immersed in 3 mM ethanol solution of carboxylic acid. (c) Model for the formation of self-assembled model of carboxylate at the surface of hydroxylated surface film on aluminium.

Through the project the potential candidates for hydrophobic compounds and corrosion inhibitor compounds based on alkyl and perfluoroalkyl chains were synthesized and tested on aluminium alloys. The most efficient compounds have been verified. The COR\_ID therefore addresses the basic relationships between aluminium surface and corrosion inhibitors, i.e. corrosion inhibitors were designed in such a way to allow the investigation of the effect of anchor group and the effect of backbone chain on their inhibitive performance on alu-

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minium in chloride solution. Methodological approach was versatile: (i) synthesis or purchase of organic inhibitors, (ii) preparation of uncoated and inhibitor-coated aluminium samples, (iii) electrochemical measurements, (iv) water contact angle measurements (v) long-term immersion tests, (vi) surface analytical study by SEM, ToF-SIMS or XPS, and (vii) Density Functional Theory (DFT) modeling. Pilot device for large-scale testing of multifunctional coatings is under construction. It will enable the on-site testing of developed coatings. The most corrosion resistant hybrid matrix has been hitherto tested in field marine environment during 8 months exposure.

During the lecture most important results obtained in the course of the projects will be summarized and presented [1-6].

**Acknowledgments:** This work is a part of M-ERA.NET project entitled “*Design of corrosion resistant coatings targeted for versatile applications*” (acronym COR\_ID). The financial support of the project by MESS (Ministry of Education, Science and Sport of Republic of Slovenia), ANR (The French National Research Agency) and NKFIH OTKA (National Research Development and Innovation Office, Hungary) is acknowledged. Région Ile-de-France is acknowledged for partial support of the ToF-SIMS equipment.

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# Local electrochemical and surface analytical analysis of corrosion and Cr(VI)-free protection of AA2024-T3

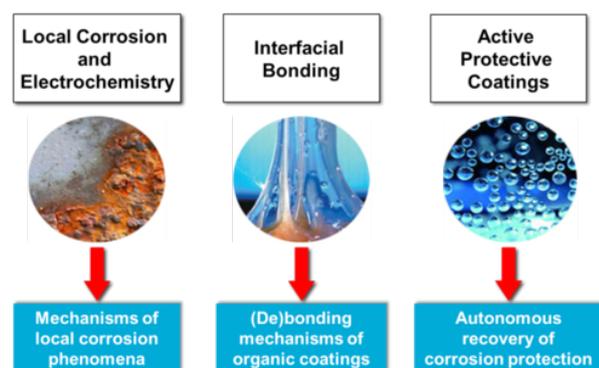
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The type, concentration, clustering and distribution of alloying elements in an aluminium matrix largely determine the mechanical and corrosion properties of the resulting alloy. Furthermore, common processing operations such as welding, chemical and thermomechanical treatments may result in a strong change in the surface microstructure of aluminium alloys. The differences in electrochemical properties of microstructural features in aluminium alloy surfaces are commonly the triggering and controlling factors in their localized corrosion behaviour [1]. However, to date we still struggle to fully bridge the gap between microstructural and electrochemical characterization at the (sub)micron scale.

During the last decades, the research field of corrosion technology and electrochemistry is experiencing a scientific revolution due to the development of local probe techniques, which enables the study of the relation between microstructure and corrosion properties at the micron scale. While the historic development of corrosion science started with a simple deterministic and thermodynamic local approach of the phenomena observed, ironically the theoretical quantitative back-up of the phenomena did become possible only after the development of the mixed potential theory, which included the kinetics, but did average out the current density over the full surface area of samples, rendering quantitative interpretation of real local phenomena as pitting, (micro)galvanic corrosion etc, virtually impossible. Local probe techniques do combine the best of both worlds: local information including the kinetics.

For systems that operate at this nanoscale, such as electronic devices, MEMS and NEMS, the need for submicron scale electrochemical analysis is obvious. For larger systems, corrosion at the nanoscale is involved in at least two key issues. First, corrosion prevention must include means to prevent the initiation of corrosion, and corrosion initiation takes place at the nanoscale. Second, the size of surface defects susceptible to trigger localized corrosion decreases as the design life-time of (high-purity) metal-based structures increases. Defects of nanometric dimensions become more important.



To protect corrosion susceptible aerospace aluminium alloys to date, hexavalent chromium (Cr(VI)) containing compounds are added in surface treatment and corrosion protection schemes, such as pretreatment layers and organic coatings, demonstrating exceptional performance in adhesion properties and active corrosion protection of metals in a wide variety of industries such as aerospace, building and automotive applications. However, the health issues associated with the use of chromates have become increasingly highlighted and are subject to strict international regulations these days [2].

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New high-potential environmentally-friendly and non-toxic alternative processes and their effect on corrosion protection and subsequent coating and adhesive bonding processes will be presented. Despite widespread investigations over the past decades, the adhesion between metals and polymers (organic coatings and adhesives) and the loss of adhesion in the presence of an aqueous environment are still subject to further scientific challenges. Both a fundamental investigation at the molecular level, using model molecules simulating the functional groups of organic coatings, and a macroscopic view on adhesion and corrosive de-adhesion on a variety of tailored base metal/metal oxide surfaces is crucial. The pivotal importance of the control of both the surface chemistry and morphology on interfacial bonding strength and durability will be highlighted [3].

Furthermore, many different compounds have been studied to find a non-toxic and environmentally friendly alternative for hexavalent chromium based corrosion inhibitors in active protective coatings for aerospace industry by rapid screening techniques and more in-depth mechanistic studies. Over the recent years, lithium-salts have become of interest as a potential alternative for chromates as leaching corrosion inhibitor in organic coatings and demonstrated active protective properties on AA2024-T3. Further insights into the active protective mechanism of the lithium-based inhibitor coating technology will be presented. The results show the mechanistically different behaviour of the lithium inhibitor doped coating technology compared to other inhibitors and demonstrate the key characteristics that are essential for active protective coatings, providing fast leaching, effective inhibition and formation of an irreversible protective layer in the defect area [4-5]. Furthermore, novel self-healing coating concepts will be presented, combining inhibitor leaching and defect closure and sealing [6].

Overall, this presentation will focus on the (im)possibilities, application areas and research challenges we face for local and in-situ electrochemical probe techniques and also novel and near future advanced techniques for in-situ corrosion, interfacial bonding studies and coating performance assessment as well as (quasi) in-situ TEM microstructural and corrosion analysis.

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# Molecular modeling of corrosion inhibitors and a search for physically sound corrosion inhibition descriptors

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Molecular modeling, based predominantly on the use of DFT methods, has become very fashionable for exploring new potential corrosion inhibitors. Within this presentation various approaches that are used to model organic corrosion inhibitors on the molecular level will be presented [1]; these include:

1. molecular-electronic-properties to inhibition-efficiency correlation (MEPTIC) approach;
2. machine-learning approach
3. explicit modeling of interactions between components of corrosion system on the nanoscale level
4. multi-scale modeling utilizing the ICME (integrated computational materials engineering) paradigm; it should be noted that this is an emerging approach, which is currently at the level of suggestions on how to implement it in the field of corrosion inhibitors.

The most proliferating among these approaches is the MEPTIC approach, which relies on the correlation between calculated molecular electronic parameters and experimentally measured inhibition efficiency. Although in many cases the correlation between molecular electronic parameters and inhibition effectiveness was claimed to be established, many purported correlations were obtained on a very small set of homologous or very similar molecules. This approach was criticized by Kokalj [2] on conceptual grounds and later by Breedon et al. [3] and Winkler et al. [4] on statistical grounds, who demonstrated that for a large data set of corrosion inhibitors the correlation between inhibitor's frontier orbital parameters and inhibitor efficiency disappears.

Despite many attempts aimed toward a more rational design of new corrosion inhibitor molecules with potentially superior corrosion inhibition characteristics there exists a formidable obstacle that hinders the development of such rational design. Namely, it appears that it is currently not known what makes a good inhibitor in terms of (molecular) physico-chemical properties and how a good inhibitor differs from a bad inhibitor.

Within this presentation we will describe our efforts in this direction undertaken within the COIN DESC project. To this end, we have tested about two dozen of differentazole molecules as potential corrosion inhibitors for copper, zinc, and their alloys in NaCl solution by electrochemical methods, such as polarization resistance and electrochemical impedance spectroscopy. Furthermore, the interfacial bonding of inhibitors was also investigated by FTIR, XPS, AFM, and STM techniques as well as by explicit DFT inhibitor-surface calculations. We aim at integrating high-throughput oriented experimental testing of a larger number of

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corrosion inhibitors with insights provided from more detailed mechanistic analyses (experimental and computational) with the specific objective to identify physically-sound corrosion inhibition descriptors.

**Acknowledgments:** This work is a part of M.Era-Net project entitled “*Coin Desc: Corrosion inhibitor and dealloying descriptors*”. The financial support of the project by MESS (Ministry of Education, Science and Sport of Republic of Slovenia), NWO (Nederlandse Organisatie voor Wetenschappelijk Onderzoek), FWO (Research Foundation Flanders), and MINECO (Ministry of Economy and Competitiveness) is acknowledged.

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# Hybrid sol-gel coatings for corrosion protection of aluminum alloys

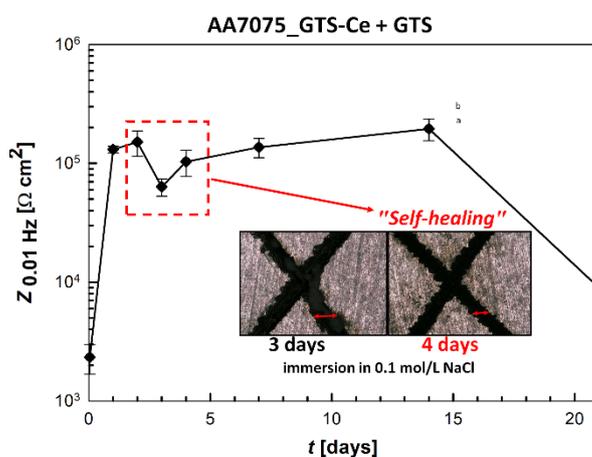
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Aluminum alloy AA7075 is most commonly used in transportation industry. Due to the presence of intermetallic particles it is susceptible to localized corrosion. Hybrid sol-gel coatings are amongst the most promising and environmentally friendly replacements for toxic chromate conversion coatings (CCCs) for corrosion protection of aluminium alloys. They combine inorganic and organic components; the former offering good mechanical properties, and the organic components increasing the flexibility and ductility of coatings, with decreased treatment temperature. In the present work hybrid sol-gel coatings, based on silane precursors 3-glycidyloxypropyl(trimethoxysilane) (GPTMS) and tetraethoxysilane (TEOS) were used as corrosion protection of AA7075. To enrich the barrier properties of coating, SiO<sub>2</sub> nanoparticles were added to the final solution. Inhibition and self-healing effect were achieved by the incorporation of corrosion inhibitor cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub>) into the coating. Due to oxygen reduction on cathodic sites OH<sup>-</sup> ions causing the local increase in pH thus enabling the precipitation of cerium oxide/hydroxide. Ce<sup>3+</sup> ions can further oxidize into Ce<sup>4+</sup> ions and insoluble Ce(IV) oxide/hydroxide may be formed to protect cathodic sites [1]. A bi-layer system of two sols was applied on the AA7075, where the first layer was doped with Ce(NO<sub>3</sub>)<sub>3</sub> and the second was undoped. Self-healing effect of coatings was studied by immersion of unscribed and scribed coated substrates in 0.1 M NaCl, by using different techniques such as immersion test, electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) with chemical analysis (EDS).

According to the EIS and immersion test, self-healing effect was effective at the scribed coating after 4 days of immersion in 0.1 mol/L NaCl [2] (Fig.1). The presence of Ce<sup>3+</sup> and Ce<sup>4+</sup> ions was confirmed with XPS analysis [2].



**Figure 1.** The impedance at 0.01 Hz for scribed GTS-Ce+GTS coating deposited on AA7075 after various immersion times and its optical images after 3 and 4 days of immersion test in 0.1 M NaCl.

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# AFM characterization and force measurements on inhibitor-modified Cu and Cu-Zn surfaces

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Materials degradation of alloys by corrosion is a potent force that destroys every year more than 3% of the world's GDP. Therefore, minimization and prevention of corrosion, e.g. by using organic inhibitor molecules, and its study on nanoscale level is an important goal. Imidazole-based inhibitors are inhibitors used for copper and copper-based alloy surfaces [1]. A complete understanding of corrosion mechanisms and protection requires this phenomenon to be studied both at the macroscopic and nanoscale level. The latter is particularly important when dealing with the early stages of corrosion. Corrosion initiation processes can be triggered by controlling the spatial distribution and molecular organization of self-assembled monolayers (SAM) of organic of inhibitors [2,3]. The spatial distributions and stability of the inhibitor layer play an important role in corrosion initiation and development. A detailed knowledge of the mechanical properties and intermolecular forces between the inhibitor layer and the metallic surface will be very helpful to unravel the mechanisms driving corrosion initiation and protection.

In this work, we use atomic force microscopy (AFM) to examine the stability and intermolecular forces of three different types of imidazole molecules, namely, 1-methyl-2-mercapto-imidazole (SH-ImiMe), 5-methoxy-2-mercapto-benzimidazole (SH-BimH-5OMe) and 5-amino-2-mercapto-benzimidazole (SH-BimH-5NH<sub>2</sub>). Self-assembled monolayers (SAMs) were formed on ultraflat polycrystalline Gold (Au) as a model surface, on polycrystalline Copper (Cu), and on a polycrystalline Cu-Zn alloy surface. SAMs were formed either by solution adsorption or microcontact printing ( $\mu$ CP), or by a combination of both [3]. The inhibitor modified metallic surfaces were characterized by topographical imaging and by tip-sample force measurement mode using AFM. Two different AFM probes, silicon and gold-coated tips were used to study the interaction forces between the sample and the AFM tip. Topographic AFM images confirmed the presence of SAMs on the surface and resolved microcontact printed topographies. In complex bottom-up build inhibitor films, i.e.,  $\mu$ CP- SH-ImiMe backfilled with 1-butanethiol, interesting molecular rearranging and film crystallization phenomena were observed. Force measurements revealed that inhibitor-modified surfaces display smaller tip adhesion as compared to their bare (unmodified) counterparts. In addition, the size of the molecular inhibitor layer can be estimated during compression upon tip approach. Significant differences appeared in terms of tip-sample intermolecular forces using Au tips between methoxy and amino-terminated inhibitor layers. Preliminary results show the presence of unbinding events upon Au tip retraction, especially on amino-terminated inhibitor-covered surfaces. Real-time in-situ electrochemical imaging by AFM on inhibitor-modified surfaces is the next step to follow corrosion in real-time.

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## Metallic glasses properties and corrosion performance

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Metallic glasses are metastable materials obtained by rapid quenching from the melt. Metallic glasses share many properties with other glasses, such as silicate-based and organic glasses. However, the basic structural unit of metallic glasses are the individual atoms and thus features related to the anisotropy of the glass structural units are not present. Therefore, metallic glasses features are due specifically to their topologic disorder. This makes metallic glasses very interesting materials to analyze the intrinsic characteristics of glasses.

Metallic glasses can be produced in ribbon form, by melt spinning, or bulk form by mold casting. Metallic glasses have interesting mechanical and magnetic properties, depending on their composition. However, as metastable materials metallic glasses are in continuous evolution. The stability and aging effects of metallic glasses are thus subject of considerable research interest.

An essential aspect of metallic glasses stability is their chemical stability, directly related to their corrosion resistance. They exhibit a chemically homogeneous nature due to the fast solidification process, which retains a disordered structure resembling the liquid. Thus, they have no structural defects like grain boundaries, twins and other lattice faults in crystalline metals, and also no compositional heterogeneity. Though the specific corrosion resistance of metallic glasses depends on their chemical composition, in many cases is better than that of their crystalline counterparts. In the particular case of Fe-based metallic glasses, low Cr addition increases allows to obtain corrosion resistance similar to that of crystalline steels with much higher Cr concentration. However, Cr reduces the glass forming ability, which is an undesired effect.

The production method of the glass has also influence in the corrosion behavior. In the case of ribbons, for example, their surface solidified in contact with an inert gas shows higher corrosion resistance than that solidified in contact to the wheel side as it has been observed in CuZr metallic glasses. This and other relevant aspects will be discussed.

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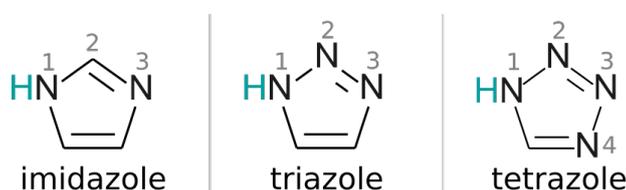
# New insights into adsorption bonding of imidazole on surfaces of metals

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Azoles—five-membered heterocyclic molecules containing one or more nitrogen atoms—are well known corrosion inhibitors for copper. Although inhibitor–surface bonding is far from synonymous with inhibition of corrosion, it is nevertheless widely accepted that adsorption of inhibitor molecules represents an important step in achieving inhibition. In a series of articles from our group [1–5], adsorption of imidazole, triazole, and tetrazole—used as archetypal models of azole corrosion inhibitors—on oxide-free [1,2] and oxidized [3–5] copper surfaces was characterized by means of DFT calculations as to provide an atomic-scale insight into the chemistry of azole–copper bonding. Two different modes of adsorption were considered, i.e., non-dissociative and dissociative, where the latter involves the abstraction of an H-atom or proton from the molecule. Considering molecular structures of the three azole molecules (Scheme 1), it seems chemically intuitive that this abstraction proceeds through the cleavage of the N1–H bond. The principle finding of the aforementioned articles is that—according to DFT calculations—all three azole molecules display similar non-dissociative adsorption energies. In contrast, significant differences between them appear for dissociative adsorption, i.e., dissociated triazole and tetrazole bind considerably stronger than dissociated imidazole, which is why dissociation via N1–H bond cleavage was found favorable only for triazole and tetrazole. While it is tempting to associate this dissociation tendency of the three molecules to their  $pK_a$  constants (i.e., imidazole is considerably more basic than triazole and tetrazole and consequently less susceptible to deprotonation), we believe that this correlation is coincidental in the current case. This tendency is instead related to the molecular geometry because triazole and tetrazole can form two strong N–Cu bonds, whereas imidazole cannot due to its “incompatible” molecular geometry.

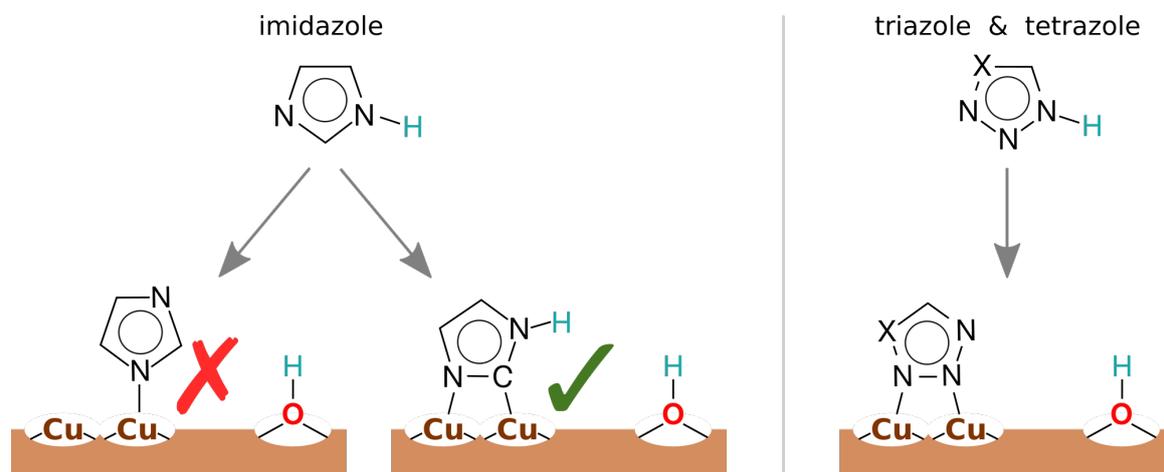


**Scheme 1.** Molecular structures of imidazole, triazole and tetrazole.

However, very recently we discovered that dissociative adsorption is favorable also for imidazole on oxide-free and oxidized copper surfaces, provided that it involves the cleavage of the C2–H bond instead of the N1–H bond. Imidazole dissociated in this way forms two strong bonds with the surface, i.e., the C2–Cu and N3–Cu bonds. Such bonding mode of imidazole was previously reported by one of us on the chemically more reactive Fe(100) surface [6], but we now find that C2–H dissociation of imidazole is favorable also on

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surfaces of Cu and Zn, but not on oxidized Al surfaces. This implies that metal d-states, even if fully occupied, are required for the C2–H bond cleavage of imidazole.



**Figure 1.** Dissociative adsorption of triazole and tetrazole involves the N1–H bond cleavage (right). In contrast, for imidazole the dissociative adsorption proceeds via the cleavage of the C2–H bond, whereas the N1–H bond breaking is unfavorable (left).

## References

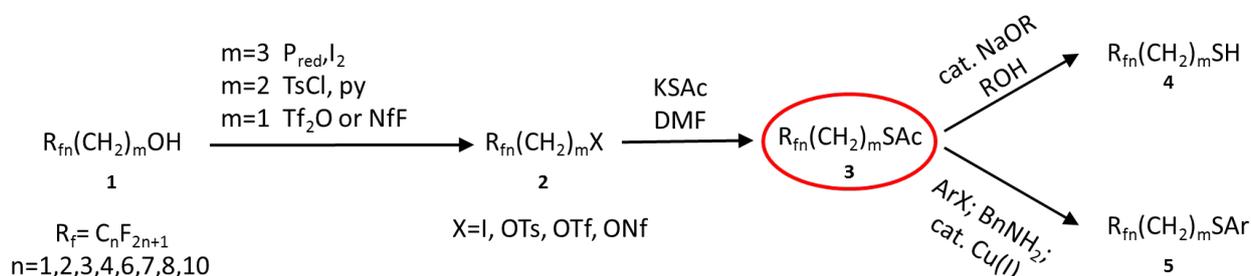
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# Preparation of (perfluoroalkyl)alkane thioacetates and their use in organic synthesis and corrosion research

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Convenient and robust synthesis of (perfluoroalkyl)alkane thioacetates, (**3**) was developed starting from commercially available fluorinated alcohols (**1**). The intermediate (perfluoroalkyl)alkyl iodides and sulfonates (**2**) were reacted with potassium thioacetate in DMF to obtain the corresponding fluorinated compounds (**3**). They can be deacetylated by a Zemplén analogue reaction [1] affording (perfluoroalkyl)alkane thiols (**4**). The latter fluorinated alkane thiols are disclosing amphiphilic properties, thus they can be used as surface treatment agents for metals or as precursor compounds for the synthesis of (perfluoroalkyl)alkyl aryl sulfides (**5**) [2].



**Figure 1.** Preparation of (perfluoroalkyl)alkane thioacetates and their transformation into thiols or (aryl) thioethers.

## Acknowledgement

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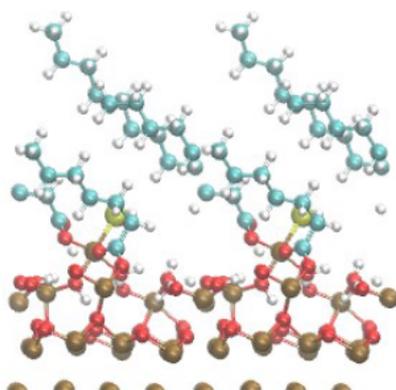
# DFT modeling of the protection of aluminum by carboxylates against adsorption and diffusion of chloride

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Because of the restrictions imposed on the use of the chromates in industrial applications, intense research efforts are being undertaken to find new environmentally friendly compounds as corrosion inhibitors of aluminum and its alloys. Linear carboxylic acids (CAs:  $C_nH_{2n+1}COOH$ ) can form stable organic green layers on the surfaces and could act as effective corrosion inhibitors of aluminum and aluminum alloys. The presence of the organic film could enhance the barrier properties of the oxide-hydroxyl film formed naturally on the surfaces. In fact, it was demonstrated that the presence of the organic layer may prevent the cathodic reactions of dioxygen reduction reaction [1].

In the present work we have studied the possible protective effect of the organic layer against adsorption and diffusion of chlorides through the organic layer to the aluminum surface (see Figure 1) using dispersion corrected density functional theory (DFT-D) and climbing image nudged elastic band (cNEB). We were interested in the case of Caproic acid ( $CH_3(CH_2)_4COOH$ ) and Lauric acid ( $CH_3(CH_2)_{10}COOH$ ) at coverage of 2.35 molecules/nm<sup>2</sup>. First, a perpendicular orientation of the organic layer to the surface was considered. For both molecules, chloride diffusion across the organic film towards the surface occurs without activation barrier, however when adding an implicit solvent (water), an activation barrier was identified in the case of Lauric acid but not of Caproic acid. For Lauric acid in a tilted orientation, chloride diffusion across the organic film is an activated process, without and with implicit solvent.



**Figure 1.** Model of Al covered with an oxide-hydroxyl film, and a layer of Lauric acid. A Cl ion is present at the oxide surface.

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# DFT modeling of passive films on Al and AlCu alloys, role of defects and corrosion inhibition

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The performance of Al and Al-Cu alloys may be strongly influenced by the different properties of the oxide layer covering the alloy (thickness, composition, hydroxylation, defects). In turn, the properties of the oxide films may be influenced by the chemical composition of the underlying metallic layers. To better understand the interplay between the structure and chemistry of passive films at the nanoscale and the resulting corrosion resistance properties, we have performed atomistic modeling of passive films properties of Al alloys using first principles calculations (Density Functional Theory, DFT). In all our works, the electronic work function was shown to be a good indicator for the cathodic oxygen reduction involved in the corrosion process and is used to characterize the effect of oxide films and organic molecules on the cathodic reaction [1-3].

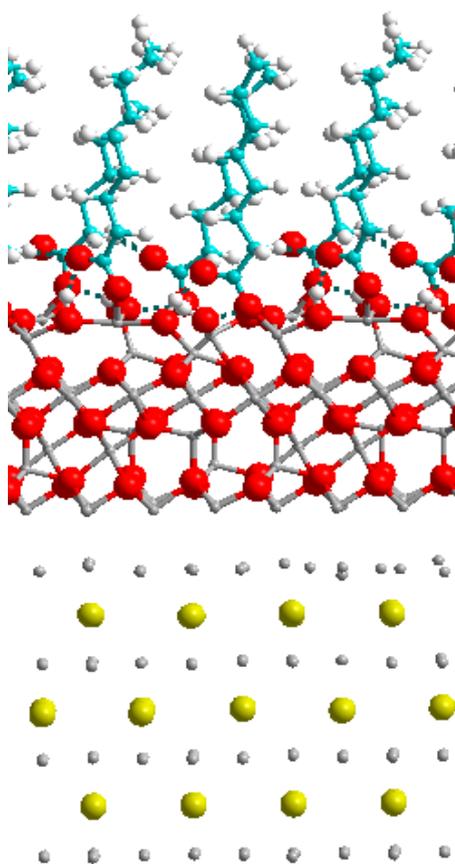
In the early stage of corrosion of Al or Al alloys (i.e., during the initiation of localized corrosion), an oxide film is generally present on the surface. We investigated the possibility for a cathodic reaction to occur on these oxide films. We discuss realistic models of supported oxide films on Al(111) in order to disentangle the factors determining the reactivity towards  $O_2$ . Three components of the complex film formed on Al(111) can be identified: an ultrathin under-stoichiometric  $Al_xO_y$  interface layer, an intermediate  $Al_2O_3$  phase with  $\gamma$ -alumina structure, and an hydroxylated AlOOH surface termination with boehmite structure. The electron transfer to  $O_2$  molecules depends on the workfunction,  $\Phi_e$ , of the metal/oxide interface and on the thickness of the inner  $Al_2O_3$  phase. The electron transfer takes place both from the metal-oxide interface and the oxide surface to the adsorbed  $O_2$  molecule. These reactions take place only when the internal alumina phase is ultrathin (here 0.2 nm). As soon as an  $Al_2O_3$  inner layer develops (film thickness higher than 1 nm), the film becomes unreactive and passivates the Al(111) surface.

Recently, several types of passive films on Al and Al-Cu alloys have been modeled, with several Cu concentrations at the interface with the oxide. At low (respectively high) concentration, Cu segregates in the first (respectively second) metal layer underneath the passive film. The Cu monolayer is the most stable configuration. A low (respectively high) Cu concentration induces the electronic workfunction increase (respectively decrease) as compared to pure Al. In contrast, without oxide, Cu segregation at the Al surface induces no workfunction change at low concentration and an increase of 0.3 eV of the workfunction at high concentration. Thus, the presence of oxide modifies the expected tendency of workfunction increase by adding a more noble metal.

Oxygen vacancies are suspected to play a significant role in corrosion initiation. Here, we studied the formation of vacancies in the passive films at different locations (metal/oxide interface, in the oxide film and in the hydroxylated film), and their influence on the electronic properties. Vacancies are stabilized at the metal/oxide interface, and induce a workfunction lowering, that favors the oxygen reduction reaction. Oxygen vacancies also favor the penetration of chlorides in the passive film.

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Finally, we analysed both experimentally and theoretically the adsorption of linear aliphatic carboxylic acids (CAs), octanoic ( $\text{CH}_3\text{-(CH}_2)_6\text{-COOH}$ ), lauric ( $\text{CH}_3\text{-(CH}_2)_{10}\text{-COOH}$ ) and stearic acid ( $\text{CH}_3\text{-(CH}_2)_{14}\text{-COOH}$ ) which are potential candidates for the corrosion inhibition of aluminium and aluminium alloys. Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS) were used to investigate the adsorption of CAs on the surface. DFT calculations allow to understand the molecule-surface interaction, and to describe the electronic properties of the organic layer. The SAMs have only a moderate impact on the electronic  $\Phi_e$ , with an increase of 0.1 eV with respect to the non-treated surface. Some attempts to model the hydrophilic/hydrophobic character of the organic layer through implicit solvent treatment will also be shown.



**Figure 1.** Summary of the modeling approach presented: the tuneable model includes: a metallic zone, an oxide/metal interface, an  $\text{Al}_2\text{O}_3$  oxide film, a hydroxylated surface zone, and an organic layer. Defects can be introduced.

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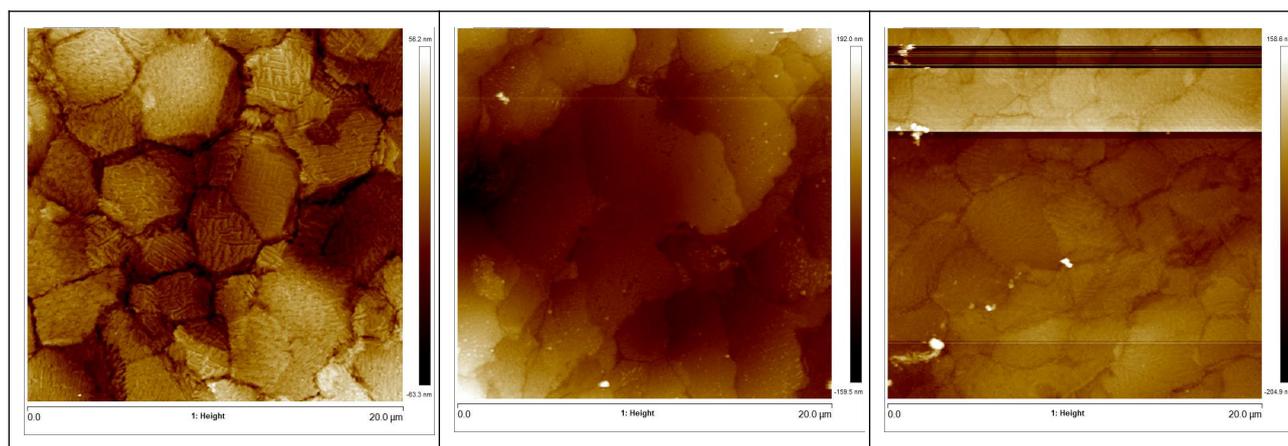
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# AFM and potentiodynamic analysis of melt-spun Cu(Zn,Zr) under corrosion agents

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Melt spinning quenching allows the easy production of metallic alloys, both amorphous and crystalline. This allows one to explore the corrosion and corrosion inhibition process in metastable metallic alloys. Melt spun samples of  $\text{Cu}_x(\text{Zn,Zr})_{100-x}$  were produced and their corrosion behavior in presence of corrosion inhibitors was analyzed by Atomic Force Microscopy and potentiodynamic measurements.  $\text{Cu}_x\text{Zn}_{100-x}$  alloys are crystalline but  $\text{Cu}_x\text{Zr}_{100-x}$  are amorphous in a wide range of compositions ( $x \in [25,70]$ ). The morphology of the untreated samples changes depending on the composition and, in the case of Zr, if the resulting alloy is crystalline or amorphous. However, the resulting samples have an intrinsic roughness due to the production process, which allows only obtaining tapping mode images and makes difficult the analysis of the AFM data. Nevertheless, changes in the surface topology can be tracked through the corrosion process and the surface state can be related to the corrosion inhibitors' efficiency. As an example, Figure 1 shows images of commercial brass after immersion in 3% weight NaCl solution with and without 4-Phenylimidazole-2-thiol, showing that the surface morphology is more similar to that of the untreated surface in presence of the inhibitor. The corrosion inhibitors' efficiency was also determined. The differences in corrosion efficiency in Zr-based amorphous and crystalline alloys will be discussed, as well as those between Zr-based and Zn-based.



**Figure 1.** AFM images of commercial brass ( $\text{Cu}_{70}\text{Zn}_{30}$ ). Left: untreated surface. Center: Surface after 24 h immersion in 3% weight NaCl solution. Right: Surface after 24 h immersion in 3% weight NaCl solution and 4-Phenylimidazole-2-thiol 1mmol.

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# Scrutinizing the bonding of 2-mercaptobenzimidazole on Cu(111) by STM and DFT

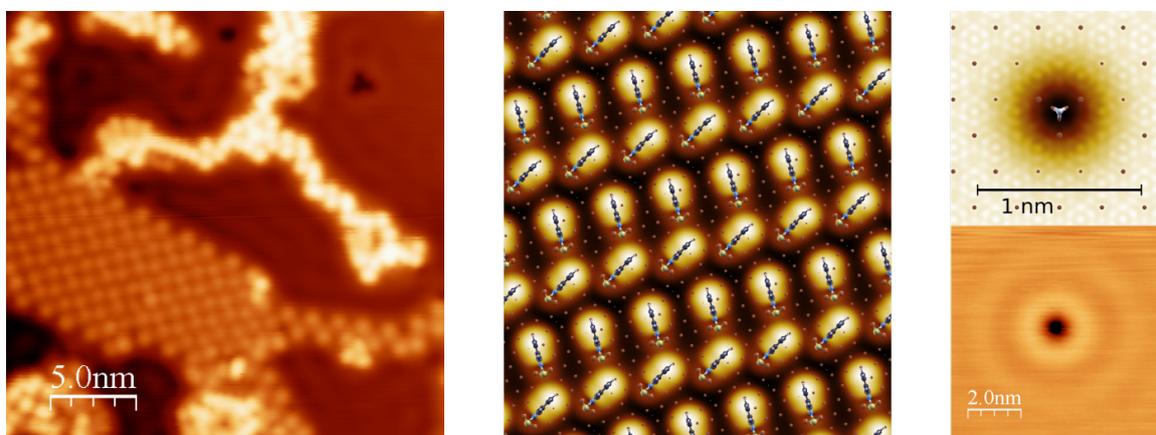
Marion van Midden,<sup>\*,1</sup> Matic Lozinšek,<sup>\*,2</sup> Erik Zupanič,<sup>1</sup> Anton Kokalj<sup>2</sup>

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Interfacial structure resulting from the interaction between Cu(111) surface and a well-known corrosion inhibitor 2-mercaptobenzimidazole [1] was investigated by a combined experimental and computational-modeling approach employing a scanning tunneling microscopy (STM) and density functional theory (DFT), respectively.

For STM studies the molecules were deposited (via evaporation) on atomically flat clean Cu(111) substrate in ultra-high vacuum. Varying the deposition rate and substrate temperature resulted in different self-assembled structures on the surface (Figure) which were studied using a Nanonis JT-STM operated close to liquid helium temperatures. Spectroscopy measurements taken on different compositions of molecules clearly show strong coupling with the substrate resulting in smeared HOMO and LUMO orbitals.



**Figure.** Left: STM topography image of different self-assembled structures that form upon vapor deposition of 2-mercaptobenzimidazole on a clean Cu(111) held at 150 K. The image is taken at 250 mV bias which corresponds to empty states. Middle: The simulated STM image at 250 mV bias with superimposed structural model. Right: The simulated STM image of an adsorbed H-atom (top) and an STM image of a mobile adsorbate (bottom).

Several different models of 2-mercaptobenzimidazole bonding to the Cu(111) surface have been evaluated by DFT calculations. These included the intact and dissociated form of the inhibitor. The intact inhibitor with molecule oriented perpendicular or parallel to the Cu(111) and bound to copper surface via S-atom was employed in its thione tautomer form, which is known to be more stable as standalone and also in the adsorbed form [2]. The dissociated form of the inhibitor with molecule oriented perpendicular to the Cu(111) and bound to copper surface via both N- and S-atoms was found by calculations to be energetically the most favorable. According to DFT calculations the barrier for dissociative adsorption via N–H bond cleavage is low enough to occur at room temperature [2]. The resulting H-atom adsorbed on the Cu(111) surface appears as a black dot on simulated STM image (Figure). The plausibility of the dissociated model is thus corroborated with the observation of very mobile adsorbates, visible as depressions in STM measurements.

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## XPS analysis of aluminium samples exposed to organic molecules and saline water

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Etched aluminium samples were immersed 30 min in 5 mM ethanol solution of organic molecules. XPS and ToF-SIMS analyses were carried out in order to determine which molecules were fixed on the surface. Samples coated with organic molecules were then exposed 6 months in NaCl and a surface characterization was carried out to understand surface modifications.

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## **Abstracts – Tuesday 12 June**

## A new experimental platform for surface science and corrosion studies

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In this talk, a new multi-technique, multi-environmental platform for spectroscopic, microscopic and electrochemical analysis of surfaces will be presented. It allows us to do *in situ* XPS on samples exposed to gases at different temperatures ranging from RT to 900 °C, *in situ* STM under gas at variable temperatures ranging from RT to 600 °C, and electrochemical measurements (CV, EIS, EC-STM), with transfers of samples in a closed system.

The research topics for this platform are the following:

- Surface nanostructures
- Surface oxide layers and passive films on metals
- Mechanisms of initiation of localized corrosion
- Corrosion inhibitors
- Coatings

This surface science approach will be exemplified by recent data obtained on the structure of stainless steel surfaces and the early oxidation stage studied by *in situ* XPS and *in situ* STM.

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## Aluminium on the global market

Dejan Lorber\*

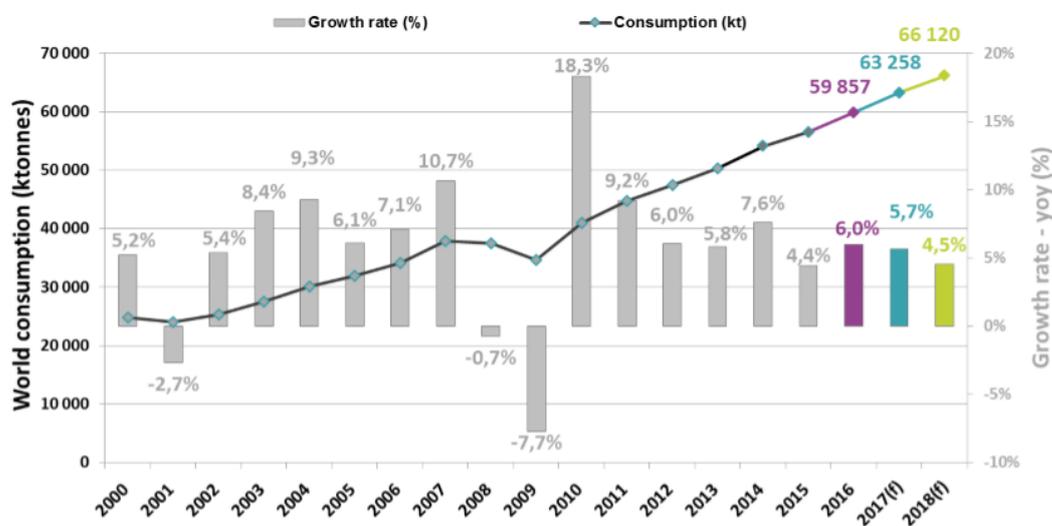
Talum d.d. Kidričevo, Tovarniška cesta 10, 2325 Kidričevo, Slovenia

After big deficit in year 2009 the production of primary aluminium is growing. Strong increase was made in 2017 and jumped from 3,1% (2016) up to 7,3%. Global aluminium consumption is expected to grow at moderate rate 3% over next 15 years. The biggest producer is China with more that 50% of world market share. Next are Middle East and North America.

The biggest consumer is still automotive industry. Transportation sector remains the key driver of aluminium demand as more innovative aluminium products and solutions are introduced. Even the weight of car is with each next model optimized, the aluminium is used for new applications. The biggest share are casted parts by 63% of total car. Other very important sectors are also construction and packaging. Due to the tight environmental standards, more secondary aluminium will be used in developed OECD countries.

The LME price of aluminium depends on situation at global market. The fact is, that China consumption is still growing but on the other increased environmental requirements cause closure of some production plants. So we can expect that the price will slightly grow in the next years.

A continuous and strong demand outlook since many years...



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# Application of surface analytical techniques XPS, SIMS and AES for corrosion studies

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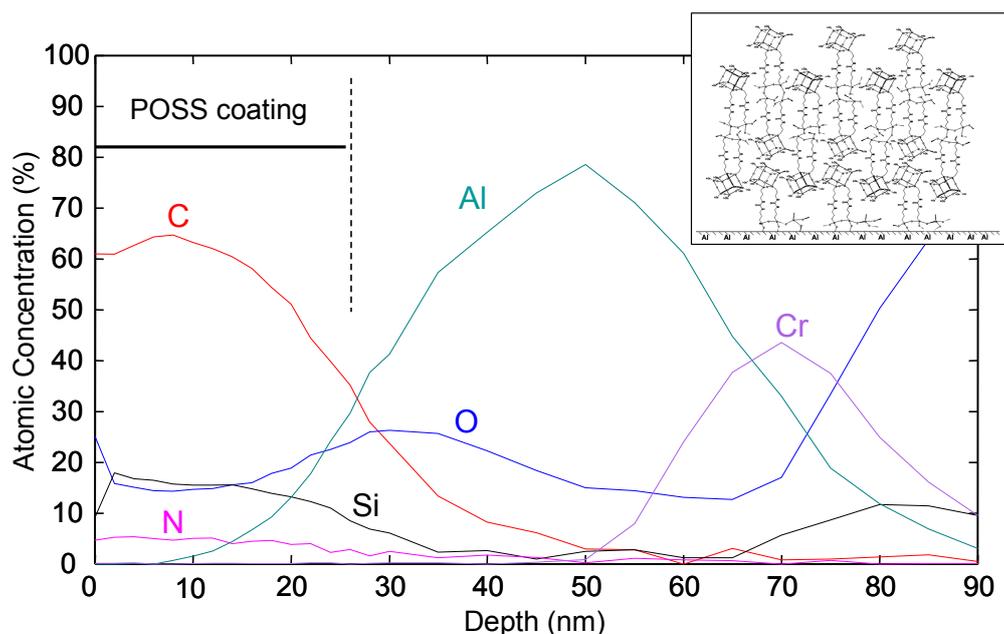
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The corrosion resistance of materials is controlled by the formation of passivating oxide surface layer, application of corrosion inhibitors and protective coatings, etc. It is important therefore to understand the processes at atomic level at surfaces and in thin films. Over the years many different techniques have been developed to probe different aspects of the surfaces and thin films. Among them X-ray photoelectron spectroscopy-XPS or ESCA, Auger electron spectroscopy - AES and Secondary ion mass spectrometry - SIMS are the most widely used surface analysis techniques which are often employed in corrosion studies. All three techniques are now available in our laboratory for characterization of surfaces, thin films and nanostructures with very high surface sensitivity (1-5 nm). The XPS method provides a data on the quantitative elemental chemical composition, identification of chemical state and bonding of elements at surfaces and in thin films. This method is non-contact and it is based on the photo effect, i.e. the irradiation of the specimen surface by a monochromatic X-ray beam and subsequent analysis of the photoelectrons emitted from the surface in ultra-high vacuum. Similar method is AES spectroscopy which is based on emission of Auger electron and may be applied on conducting materials at high lateral resolution down to few nm. Secondary ion mass spectrometry - SIMS, is the mass spectrometry of ionized molecules and atoms, which are emitted in vacuum when a surface is bombarded by focused energetic primary ions. SIMS technique provides detailed elemental and molecular information with elemental detection limits ranging in ppm range, sensitivity for hydrogen and detection of isotopes. It is particularly suitable for characterization of surfaces of organic coatings and materials. Highly focused ion beam allows also 2D and 3D chemical and molecular imaging of the surfaces.

In this presentation some examples of XPS, SIMS and AES surface analyses in corrosion studies in particular in applications of organic corrosion inhibitors [1, 2], sol-gel coatings (Figure 1) [3], PVD coatings [4] and aspects of surface cleaning [5] on corrosion performance of materials will be presented.

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**Figure 1.** XPS depth profile of thin triethoxysilyl functionalized POSS corrosion protection coating on an Al/Cr/glass substrate [3].

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# Fluorous chemistry and fluorous surface modification

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The evolution of fluorous chemistry took a high leap after the discovery of fluorous biphasic catalysis [1]. Several synthetic organic chemistry methods, like fluorous extraction [2], fluorous mixed synthesis [3], phase-vanishing reactions [4] and fluorous solid phase extraction (*F*-SPE) were developed [5].

The first widely known fluorous surface modification was used in *F*-SPE, which method requires silica particles modified with (perfluoroalkyl)alkylsilanes as packing of a chromatography column. In the first half decade of 2000's several biological assay was developed (for proteins [6], or DNA [7]), based on fluorous-fluorous interactions. In the latter methods fluorous surface modified glass plates were used.

Today corrosion prevention of metals (Al, Mg, Zn, Cu, steel) is possible using fluorous surface modification. In most cases the modification results in superhydrophobic surface.

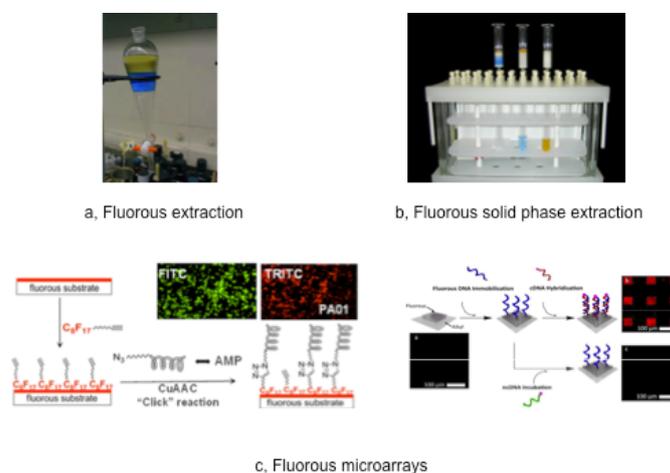


Figure 1. Fluorous extraction and microarray methods

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# Superhydrophobic coatings on aluminium based on alkyl and fluoroalkyl silanes

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Aluminium holds an important position in the modern industry because of superior physical and mechanical properties. However, when aluminium is subjected to some harsh environment such as  $\text{Cl}^-$  containing solution, it is prone to corrosion. Consequently, it is crucial to improve this drawback, which can be achieved with a surface modification to obtain superhydrophobic surface [1].

Aluminium with the superhydrophobic characteristics (water contact angle greater than  $150^\circ$  and sliding angle less than  $10^\circ$ ) has attracted tremendous attention over the last decade in both academic and industrial areas because such modified surface often shows self-cleaning and anti-icing properties [1].

Nowadays the research on the superhydrophobic surface has been mainly focused on alkyl and fluoroalkyl silanes [1, 2]. They have been widely used as surface modification agents because of their high hydrophobic properties. Coatings containing fluorochemicals with a C–F bond find applications in many fields, recently in barrier corrosion protection.

In this study, a simple procedure for preparation superhydrophobic and corrosion resistant coatings on aluminium was developed based on surface modification using alkyl and fluoroalkyl silanes. In order to investigate the effect of C–F and C–H groups on hydrophobicity and corrosion resistance molecules with different chain length were explored. The superhydrophobic coating based on fluoroalkyl silane provides a highly efficient corrosion-resistant coating during immersion in an aqueous solution of 0.5 M NaCl solution. The corrosion properties were elaborated using electrochemical measurements. The surface characterisation was performed using contact profilometer, scanning electron microscopy, IR spectroscopy and water contact angle, Fig. 1.

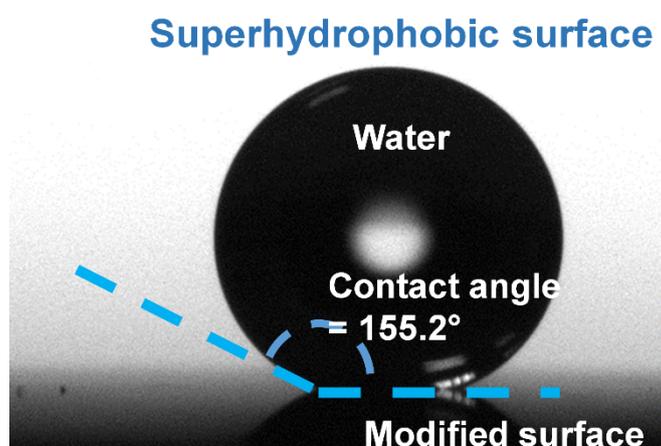


Figure 1. Water drop on the modified aluminium surface.

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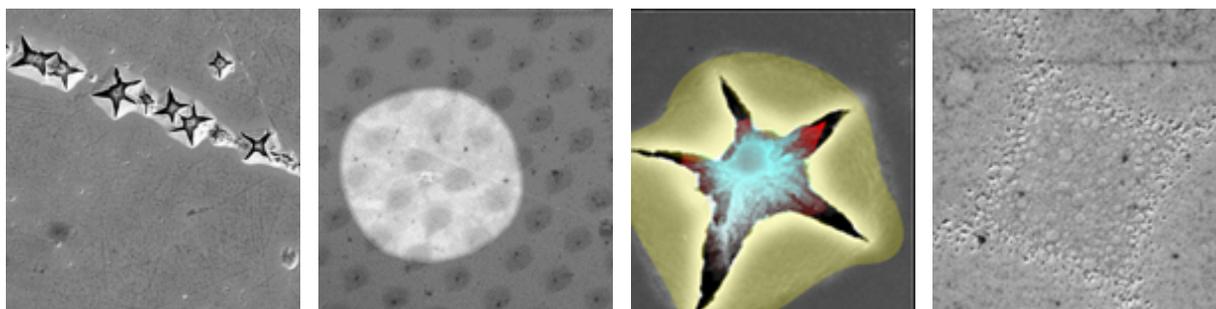
## Effect of inhibitor modifications on dealloying studied on the atomic scale: a surface science approach

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Corrosion is affecting a broad range of metallic materials, from structural steels to microelectronics or biomedical alloys, and is causing a huge amount of damage to society. Despite a substantial number of reports on corrosion testing is available, only a few projects aim to understand the basic processes driving corrosive materials degradation. Localized dealloying, a special type of corrosion, takes place on noble alloy surfaces modified with self-assembled monolayers (SAMs) of organic inhibitors [1]. Corrosion initiation at the nanoscale can be addressed by controlling the spatial distribution and molecular organization of inhibitor-molecule SAMs at nano and micro length scales. We use micro-contact printing on model ultra-flat thin film and single-crystal surfaces, such as atomically flat  $\text{Cu}_3\text{Au}$  (100) surfaces, to obtain well-defined complex organic (inhibition) layers. More complex films can be build up by following a multi-step printing approach [2]. For inhibited dealloying of  $\text{Cu}_3\text{Au}$  (100) surfaces the initiation of localized dealloying is strongly dependent on the prepared exact nanoscale surface morphology [3]. Applying a surface science approach to corrosion promises new insights in corrosion mechanisms.



**Figure 1.** Corrosion attack morphology obtained by differently prepared surfaces and thiol inhibitor micro-prints.

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# Bonding of several corrosion inhibitors to oxidized aluminum surfaces

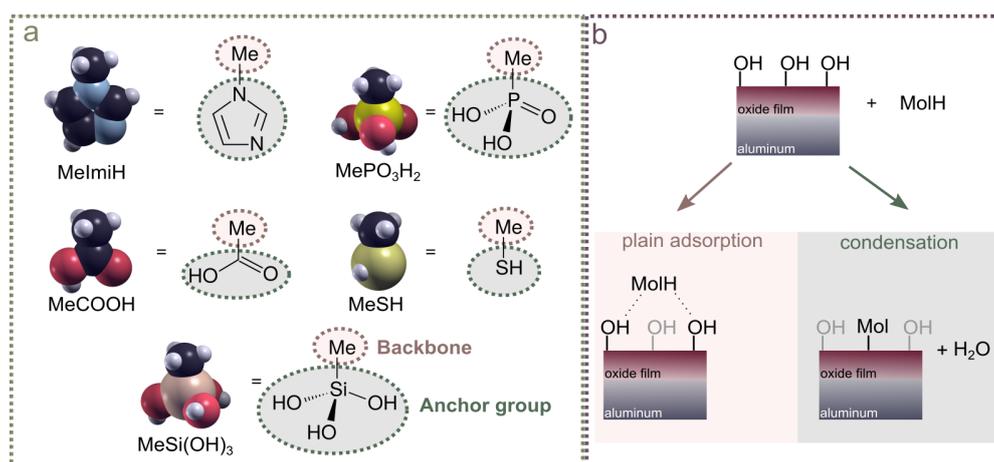
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Aluminum is a widely used metal. Its native oxide film provides good corrosion resistance in the pH range from 4 to 8. To ensure corrosion resistance under even harsher conditions, chromate based coatings were typically used, but due to their carcinogenicity alternatives are sought. In this context we have investigated the bonding of several corrosion inhibitor candidates to hydroxylated oxidized aluminum surfaces by means of Density Functional Theory (DFT) calculations. In order to scrutinize various interactions involved in the molecule–surface bonding and within the monolayer of adsorbed molecules, the molecular structure of the inhibitors is divided into two components: (i) the anchor group, which reacts with the surface, and (ii) the backbone, which determines the lateral interactions within the self-assembled monolayer (SAM). We first consider the effect of different anchor groups. To this end, a methyl (Me) group is taken as a minimum representation of the backbone. The investigated molecules are methylthiol (MeSH), 1-methylimidazole (MeImiH), methylsilanetriol (MeSi(OH)<sub>3</sub>), ethanoic acid (MeCOOH), and methylphosphonic acid (MePO<sub>3</sub>H<sub>2</sub>); their respective molecular structures are shown in Figure 1a.



**Figure 1.** (a) The structures and schematic representations of the considered corrosion inhibitors. (b) Reaction schemes depicting plain adsorption (left) and condensation (right), where MolH and Mol are used as generic labels for a non-dissociated and dissociated inhibitors.

Two different possible adsorption bonding modes were analyzed: (i) plain adsorption, where no chemical bond is broken and adhesion is achieved mainly via H-bonding to surface hydroxyl groups and (ii) adsorption via condensation, where the inhibitor molecule replaces a surface hydroxyl group and a water molecule is formed (both pathways are depicted in Figure 1b). The plain adsorption mode is exothermic for all

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considered cases. On the other hand, adsorption via condensation is endothermic for MeSH and MelmiH by 0.4 eV and 1.1 eV, respectively. This indicates that inhibitors containing these anchor groups will not chemisorb to the surface. For MeCOOH, MePO<sub>3</sub>H<sub>2</sub> and MeSi(OH)<sub>3</sub> the condensation reaction energy ( $\Delta E$ ) is exothermic; the respective values of  $\Delta E$  are -0.2 eV, -1.2 eV and -0.9 eV [1]. The bonding of both phosphonic and silanol anchor groups is therefore appreciably exothermic and inhibitors containing these groups will bind strongly to the surface, while for the carboxylic group additional stabilization via lateral interactions is required for the formation of a stable adsorbed monolayer.

As for the analysis of the effect of lateral interactions within the SAM, the methyl group in MeCOOH was replaced by alkyl chains with lengths ( $n$ ) from 2 to 17 carbon atoms. We find that the chains are tilted with respect to the surface normal. The tilting angle is such that the lateral interactions between the chains are maximized and its value depends on the nature of the surface and the steric footprint of the anchor group [2]. The dependence of lateral interactions on chain length displays bilinear behaviour, because shorter chains ( $n < 6$ ) are not long enough to achieve the optimal inter-chain distance with tilting.

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