Development of ATR-FTIR Kretschmann Spectroscopy for In situ Studies of Metal / Polymer Interfaces

and its Integration with EIS for Exposure to Corrosive Conditions

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Abstract

The environmental stability of a metal / polymer interface is essential for the durability and mechanical stability of constructions in several important areas such as the automotive, offshore, building and aerospace industries. The protective capability of a polymer film is strongly connected to its barrier properties, but the transport of water and corrosive constituents through the polymer and the subsequent processes at the metal surface are complicated to analyse in detail. The surface to be analysed is confined between two media that are impermeable to most probing particles used in conventional analytical techniques. Several methods exist to describe separate parts of the system, but few techniques work at ambient pressure and have the capacity to conduct real-time analysis at relevant exposure conditions. In this work, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) in the Kretschmann geometry was successfully employed for systematic studies of metal / polymer interfaces. This technique requires the use of thin metal films deposited on an internal reflection element (IRE). Most studies were performed on aluminium, which is an important structural light-weight material, but also zinc was analysed, being frequently used for corrosion protection of steel. Upon exposure to water and electrolytes, the ATR-FTIR Kretschmann technique was found capable to monitor and to separate early deterioration-related processes at the aluminium / polymer interface, including water sorption and transport of ionic species through the polymer film. Other main processes identified were the formation of corrosion products and swelling of the surface-near polymer network. To perform more comprehensive interpretations, a spectro-electrochemical method was further developed for in situ studies of hidden metal / polymer interfaces. The ATR-FTIR Kretschmann technique was combined with the complementary acting technique, Electrical Impedance Spectroscopy (EIS). The integrated set-up was able to provide complementary information, with ATR-FTIR Kretschmann being sensitive to the surface-near region and EIS to the whole system. For instance, metal oxidation and delamination processes can be difficult to distinguish by EIS, while on the other hand oxidation and hydration reactions on aluminium can be confirmed as IR bands at distinct positions. Delamination and swelling of a polymer both result in negative bands in an IR spectrum, but these processes may be distinguished by EIS as alterations in different frequency regions. While traditional chemical pre-treatments for enhanced hydrolytic stability perform excellent, they are being phased out from industrial applications due to environmental concerns and work health issues. Today there is an intense ongoing research regarding the mechanisms and performance of environmentally friendly pre-treatments to develop systems of similar performance, and the analysis of the confined metal / polymer interface is crucial for this development. The capability of the integrated in situ ATR-FTIR Kretschmann and EIS set-up was therefore further applied to systems where a surface pre-treatment had been applied to the metal prior to organic coating. Studies were performed on vacuum-evaporated films of zinc treated with a titanium-based conversion coating and coated with a UV-curing polymer. Alterations of the conversion layer could be detected upon exposure to the electrolyte. Also alkaline-cleaned aluminium coated with an amino-functional silane film and a thermo-curing epoxy top-coat was thoroughly characterized by both ATR-FTIR and IRRAS, and further investigated upon exposure to electrolyte and humid air. Changes at the hidden interface were detected upon thermal curing of the epoxy film and during exposure in electrolyte, and the in situ ATR-FTIR Kretschmann analysis showed a high sensitivity towards alterations in the interfacial region. Complementary studies in the absence of metal could confirm a water uptake within the silane film and water-induced alterations of the siloxane network.
List of Publications

I. **In situ ATR-FTIR studies of the aluminium / polymer interface upon exposure to water and electrolyte**
   Maria Öhman, Dan Persson and Christofor Leygraf
   Progress in Organic Coatings, 57 (2006) 78-88

II. **A spectro-electrochemical study of metal/polymer interfaces by simultaneous in situ ATR-FTIR and EIS**
    Maria Öhman, Dan Persson and Christofor Leygraf

III. **An integrated in situ ATR-FTIR and EIS study of buried metal / polymer interfaces exposed to an electrolyte solution**
     Maria Öhman and Dan Persson

IV. **In situ studies of conversion coated zinc / polymer surfaces during exposure to corrosive conditions**
    Maria Öhman, Dan Persson and Dan Jacobsson
    Accepted for publication in Progress in Organic Coatings

V. **ATR-FTIR Kretschmann spectroscopy for interfacial studies of a hidden aluminium surface coated with a silane film and epoxy.**
   I. **Characterisation by IRRAS and ATR-FTIR**
      Maria Öhman and Dan Persson
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VI. **ATR-FTIR Kretschmann spectroscopy for interfacial studies of a hidden aluminium surface coated with a silane film and epoxy.**
    II. **Analysis by Integrated ATR-FTIR / EIS during Exposure to Electrolyte with Complementary Studies by in-situ ATR-FTIR and in-situ IRRAS**
       Maria Öhman and Dan Persson
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Author Contributions

The work was planned together with the supervisor Dan Persson and performed by the author. The manuscripts were mainly written by the author in close co-operation with the supervisor / co-author.

All experimental work was performed by the author, except for the coating-application in Paper IV, the GDOES analyses in Papers IV and V, and the EDX analysis in Paper V. The calculated spectra presented in Paper V were derived by the supervisor / co-author.
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Papers I-VI
1. Introduction

1.1. Background and purpose of the study

The most common mechanisms for deterioration and structural failure of polymer-coated metals and adhesively bonded metal structures are triggered by exposures to the surrounding environment. This means that the stability of a metal / polymer interface is essential for the durability and mechanical stability in several important areas such as the off-shore, building, automotive and aerospace industries.

A major aim of applying an organic coating to a metal is to suppress electrochemical reactions at the metal surface by excluding water and other corrosive constituents. Nevertheless, water will move within a polymer film, either by diffusion through the bulk phase or by migration through pores and other defects. This makes the analysis of the hidden interface of utmost importance to secure the quality of the system. Despite great efforts made to understand the interfacial stability of a metal / polymer system, there is still a lack of knowledge regarding processes at the hidden interface and the mechanisms that destabilize the structures upon exposure to corrosive conditions. A major reason for this lack of information is that the metal / polymer interfaces are confined between two media that are impermeable to probing particles such as photons, electrons and ions. This means that the mechanisms of deterioration as well as the inhibiting behaviour of protective surface films are very difficult to evaluate.

Analysis at the hidden metal / polymer interface is also crucial for the development of novel environmentally friendly pre-treatments, where it is important to understand e.g. the nature of bonding to the metal and interactions with the organic coating, as well as the water-induced changes of the surface films and the role of corrosive constituents on the interfacial stability.

Methods exist for analysis of separate parts of these phenomena, but both the transport of water and ions to a metal / polymer interface and the subsequent processes at the metal surface are complicated to analyse in detail. Several electrochemical techniques have considerably increased the understanding of the corrosion properties of metal / polymer interfaces. Electrical impedance spectroscopy (EIS) constitutes a powerful tool for in situ monitoring of the transport of electrolyte in attached polymer films on metals, as well as of corrosion and other processes at the metal surface. The scanning Kelvin probe can be used to follow the water uptake during exposure to both water/electrolyte solutions and humid air, and can also monitor corrosion processes and local electrode potentials at the metal surface beneath the polymer film. In addition, scanning Kelvin probe force microscopy has been used to investigate the mechanisms of delamination at a polymer-coated metal surface. Solid state nuclear magnetic resonance spectroscopy and neutron reflectivity can be used to map the presence and interactions of moisture in the metal / polymer interfacial region. The transport of ions through polymers has also been analysed by molecular probe techniques, by quantitative electron probe microanalysis, and by using radioactive electrolyte solutions. Also adhesively bonded joint structures have been studied by dielectric techniques that determine e.g. the quantity and state of water within the polymer and identify hydroxide formation at the metal substrates. However, there is a need for additional chemical information from surface analytical techniques in order to unambiguously...
interpret the results. For instance x-ray photoelectron spectroscopy and time-of-flight secondary-ion mass spectroscopy have been used together with an ultra-low-angle microtome technique for composition depth profiling of attached polymer films. Cross-sections may also be prepared for transmission electron microscopy, which allows further elemental analysis with e.g. energy dispersive x-ray spectroscopy. As the use of high-vacuum techniques may cause alterations of the surface to be studied, the data obtained from an analytical technique is more reliable when working at ambient pressure. The analytical technique further benefits from the capacity to conduct in situ analysis at relevant exposure conditions.

One advantage with Fourier transform infrared spectroscopy (FTIR) over many other surface analytical techniques is the possibility to follow corrosion processes in situ under climatic conditions, both in humid air and in liquids. In the field of corrosion, FTIR is frequently used to study the corrosion product formation and the degradation of organic coatings. Infrared reflection absorption spectroscopy (IRRAS) is based on reflection of infrared radiation with a grazing angle of incidence on the metal surface. Due to the enhancement of the electric field strength perpendicular to the plane of the metal surface, IRRAS is highly surface sensitive when using polarized IR radiation and permits the analysis of very thin surface films. IRRAS may provide information about both the composition of the surface film and the bonding to the metal surface and has for example been applied for in situ studies of atmospheric corrosion. In the presence of very thin organic films, in situ FTIR micro-spectroscopy in the external reflection mode has also been applied to study the mechanisms of filiform corrosion beneath the organic film. While IRRAS is restricted to analysis of thin surface films, the attenuated total reflection (ATR) FTIR, also known as internal reflection spectroscopy, can be applied on thick films and opaque solutions. Furthermore, ATR-FTIR in the Kretschmann geometry allows surface studies of thin metal films deposited on an infrared-transparent material, and is the technique on which this work is based.

1.2. Objective

Mechanisms of deterioration and the inhibiting behaviour of protective surface films are of utmost importance but are very difficult to evaluate. This work seeks to investigate the stability of a hidden metal / polymer interface and to extract chemical information of the surface that is confined between two media. ATR-FTIR in the Kretschmann geometry has the ability to detect alterations obtained from vibrations of IR-active species such as water, polymers and certain corrosion products and ions. As the destabilisation of the interface is promoted by the ingress of water and electrolytes, a more comprehensive picture may however be obtained from combining the ATR-FTIR Kretschmann set-up with an electrochemical technique, where electrochemical impedance spectroscopy (EIS) was chosen for conducting integrated spectro-electrochemical studies upon exposure to electrolyte solutions. Analysis at the hidden metal / polymer interface is also crucial for the development of novel environmentally friendly pre-treatments, where it is essential to understand issues as the nature of bonding to the metal, the interactions with the organic coating, the water-induced changes of the surface films and the role of corrosive constituents on the interfacial stability. The capability of the experimental set-up was therefore further employed for analysis of metal / polymer systems where a surface pre-treatment was applied to the metal prior to coating.
1.3. Material aspects

1.3.1. Aluminium and zinc as construction materials

This work is based on the technically interesting metals aluminium and zinc. Aluminium is a low-density metal with good mechanical strength when alloyed. This makes it useful in a wide range of applications for example in transport, building, aerospace and off-shore applications. Today aluminium alloys are used as construction material for several car components in the advancement of the light vehicle technology. The ductility of aluminium is, on the other hand, beneficial in the flexible packaging industry, where untreated aluminium foils are coated by thin organic films. When exposed to the atmosphere, a thin continuous layer of aluminium oxide (Al$_2$O$_3$) is spontaneously formed at the surface. Normally, the oxide film formed in air at ambient temperature is only about 2.5 nm thick. This passive film is usually amorphous and immediately reforms when damaged. This makes untreated aluminium alloys relatively well protected towards further corrosion, but upon environmental exposure the formation of a weak boundary layer is considered detrimental for the interfacial stability and the adhesion to organic coatings (Figure 1.1(a))$^{26,40-43}$. In order to improve the interfacial stability, many applications require an additional chemical pre-treatment that interacts with the metal surface prior to organic coating. Zinc is a commonly used material for corrosion protection of steel by e.g. hot-dipped galvanizing (HDG) or electro galvanizing (EG) processes. All mild steels and cast irons can be hot-dip galvanized, but the thickness and structure of the coating will depend on the alloying elements. With steel and zinc in contact in the presence of an electrolyte, a current will flow to the zinc. This makes zinc the anodic electron-producing corroding area while the steel surface is protected$^{44}$. The native surface film on zinc is however considered troublesome for further adhesion to an organic coating and the zinc surface also easily form basic zinc carbonates at ambient atmosphere (Figure 1.1b). In the presence of an aggressive environment, the zinc therefore requires further corrosion protection, such as a chemical pre-treatment, prior to organic coating.

![Figure 1.1. Schematic picture of surface films commonly formed at ambient climatic conditions on (a) aluminium and (b) zinc.](image)

The surface hydroxyl groups on various metal oxides are subjected to acid-base equilibria in aqueous solutions. The isoelectric point (IEP) denotes the pH were the surfaces has no net
charge. At a pH above the IEP, the surface has a net negative charge, while at a pH below the IEP the surface charge is positive. The acid-base properties of the oxide surface are of significance for the interaction of ionic and molecular species with the oxide surface, such as the formation of silane layers on the surface and the interaction between this oxide and functional groups in organic coatings. For oxidised/hydroxylated pure aluminium, the IEP is about 8-10, but for aluminium alloys the IEP depends on the alloying elements and may be significantly lower.\textsuperscript{45,46} For zinc oxide the IEP is about 9.\textsuperscript{47}

The ATR-FTIR Kretschmann spectroscopy used as the main technique in this study requires the use of thin metal films. For this reason, model substrates of pure aluminium and zinc were produced by vacuum evaporation. Thin metal films deposited by evaporation may however have densities, optical and electrical properties that significantly differ from those of the bulk metal.\textsuperscript{34,48-50}

1.3.2. Novel chemical pre-treatments for aluminium and zinc

Organic coatings are commonly applied on both aluminium and HDG/EG steel for example in order to extend their applications by an improved corrosion resistance, for aesthetic surface finish purposes, and on for aluminium to improve its food compatibility in the packaging industry. Additionally, the interest in adhesively bonded structures is increasing, e.g. in the advancement of the light vehicle technology. Although organic coatings may provide a rather good protection, the system is not perfect. A common method to improve the hydrolytic stability of organically coated metals is to apply a chemical pre-treatment on the metal surface.

The protective properties of traditional chromium conversion coatings are superior to those of other surface treatments, with dense oxides working as a barrier towards corrosive constituents and as a repository for soluble hexavalent chromium that can be released, diffuse to a corroding site and form a passivating oxide. However, the use of hexavalent chromium is legally restricted due to its harmful effects on human health and the environment and is being phased out from industrial applications. Huge efforts are made to develop “green” inhibitors to provide interfaces of similar stability. Phosphating of aluminium and zinc provides hard, crystalline, insoluble oxides and phosphates of the metal being treated. The corrosion protection comes from the insulating nature which prevents onset and spreading of corrosion. However, also the phosphating process experiences criticism due to its environmental impact and high costs of waste treatment.

Conversion coatings with a low environmental impact may be based on for instance zirconates and titanates, which form transparent colourless films by interfacial precipitation of metal oxides and hydroxides.\textsuperscript{27,51} An oxide layer is formed by oxides of the base material mixed with precipitates of TiO\textsubscript{2} and/or ZrO\textsubscript{2}. The amount and distribution of oxide on the surface depends on the alloy composition and the electrochemical heterogeneity.\textsuperscript{51-53} The deposition mechanisms have for example been studied by scanning Kelvin probe force microscopy\textsuperscript{52} and energy dispersive x-ray spectroscopy.\textsuperscript{52,54} The composition of the thin films may be studied by x-ray photoelectron spectroscopy\textsuperscript{51,55-57} and glow-discharge optical emission spectroscopy\textsuperscript{51,54}, while thin film morphology also have been studied by e.g. spectroscopic and visual ellipsometry\textsuperscript{58}, neutron reflectivity\textsuperscript{59} and electron probe microanalysis.\textsuperscript{27} Figure 1.2 exemplifies the appearance of such conversion-coated films, first with a transmission electron micrograph of aluminium AA 6060 treated with a Ti-Zr-based
conversion solution (with preferred deposition on cathodic inclusions such as $\alpha$-AlFeSi\textsuperscript{27, 51}) and also two FEG-SEM micrographs of a HDG-steel surface, as-received and after treatment with a Ti-based conversion solution, respectively\textsuperscript{60}.

![Conversion coating](image)

**Figure 1.2.** (a) Transmission electron micrograph (cross-section) of aluminium alloy AA6060 treated with a Ti-Zr-based conversion solution\textsuperscript{27, 51} and (b) FEG-SEM micrographs of HDG-steel as-received and after treatment with a Ti-based conversion solution\textsuperscript{60}.

The insulating properties and mechanisms have been investigated by for example electrochemical impedance spectroscopy\textsuperscript{15, 61, 62} and scanning Kelvin probe\textsuperscript{15}. In order to obtain better corrosion-resistant properties, some systems also contain organic components which act as complexing agents for the inorganic components and also protect by forming a barrier layer\textsuperscript{56}. While many studies of chromium-free conversion coatings exist on aluminium substrates, fewer studies have been performed on zinc or zinc-plated steel\textsuperscript{57, 60, 63}. In the present study (Chapter 3.3.2); an aqueous conversion system based on hexafluorotitanic acid is applied on zinc substrates.

Another environmentally acceptable route is to apply adhesion promoters such as silanes to the metal substrate. Organofunctional silanes received attention in the 1940’s, as coupling agents for improving the adhesion between glass fibers and their organic resins\textsuperscript{64, 65}, and they were soon also considered for metal substrates. In contrast to the case with conversion systems, the metal does not participate electrochemically in the film deposition mechanism. Instead the silane forms an interfacial layer of covalent bridges at the interface between the alkali-cleaned metal substrate and an organic coating. The silanol groups (Si-OH) of a hydrolysed organosilane have a pH of ~2-3 and are relatively stable in acid solutions. When the pH in the solution is lower than the IEP value of the metal, these negatively charged Si-OH groups may coordinate with metal hydroxyl groups present at the metal surface (Figure 1.3). Residual silanols form a densely cross-linked siloxane multilayer that is aimed to provide further protection against hydration and the action of aggressive species. The amino-functionalities react further with the functional groups of the organic coating.
Figure 1.3. A schematic picture of silane-reactions at a metal surface, with hydrolysis of the amino-functional organosilane and subsequent condensation of the silanols at a hydroxylated aluminium surface.

The mechanism of adhesion is not well understood, and is difficult to verify by analytical tools. For aluminium substrates, the Al-O-Si$^+$ structure has been suggested from secondary-ion mass spectroscopy studies. Adsorption of silane to metal has also been verified by x-ray photoelectron spectroscopy. However, while several FTIR studies have claimed the presence of Al-O-Si linkages, these studies may be less convincing as the spectral region assigned to possible Al-O-Si linkages strongly overlaps with vibrations related to Si-O and Al-O. These studies also say little regarding film coverage and coating weight. Thin film thicknesses have been deduced by e.g. spectroscopic ellipsometry and transmission electron microscopy. Adhesion to a polymer top-coat may be the result of both physical interactions and chemical bonding through a functional end group. Due to regulations and restrictions regarding the use of solvents for industrial applications, commercial products today are commonly delivered as water-based pre-hydrolysed solutions. The corrosion resistance of a silane layer may be rather poor in itself, especially for more hydrophilic films, and it is important to obtain a film of low porosity. Also mixtures of different types of silanes may be more effective than a single silane. Several manufacturers currently also combine silanes with inorganic components and organic additives within the same product, and studies are ongoing regarding the use of active inhibiting components such as cerium and zirconium nitrates and nanoparticles of cerium oxide. In the present study (Chapter 3.3.2), a water-based mixture of two different silanes is deposited onto alkali-cleaned aluminium substrates.
1.3.3. Transport through polymer films

Water and other species will move within a polymer film, either by capillary flow (non-activated diffusion) through pores and irregularities, or through the polymer bulk phase by means of activated diffusion through holes formed as a result of segmental motion of the polymer network \(^{1-7, 41, 83-88}\). The polymer film also acts like an ohmic barrier between the anodic and cathodic sites \(^{1, 3, 6, 84-86, 88, 89}\) and the electrolytic resistance is determined by its dielectric properties.

The main sorption modes of water within a polymer network are bulk dissolution, clustering of water molecules, hydrogen-bonding to hydrophilic groups in the polymer, and adsorption onto free volume micro-voids \(^{90-92}\). At low water activities, water enters spaces that already exist in the molecular structure, and interact with polar or ionic groups in the network. At increased water activity, accumulation of water can result in an elastic stretching \(^6\). Water molecules within a polymer network are generally more weakly hydrogen-bonded than in a pure water network \(^{93}\). Due to the high degree of defects introduced in the water structure, interstitial water also appears differently from bulk water in an IR spectrum \(^{93-97}\).

The processes and properties that affect the polymer permeability and susceptibility to ageing are strongly dependent on the structural and chemical properties of the polymer. The solubility of water, the degree of swelling and the mode of relaxation are influenced by for instance the exposure time, the degree of hydrophilicity of the polymer, and the porosity of the polymer matrix \(^{6, 90, 98, 99}\). Additional factors are the curing conditions, the surrounding temperature, partial pressure and the properties of the penetrant \(^{6, 85, 100, 101}\).

For a polymer bulk phase, the flux of matter, \(J\), through a polymer film can be expressed by Fick’s first law of diffusion in terms of the concentration gradient and the diffusion coefficient, \(D\), of the penetrating medium (Eq. 1) \(^{102}\).

\[
J = -D \frac{dc}{dz} \quad \text{(Eq. 1)}
\]

For a free homogenous film of insignificant swelling, the mass uptake as a function of time may be fit to a single Fickean diffusion coefficient. The mass transport of the penetrating medium can then be given by Eq. 2, where \(L\) is the sample thickness and \(M_t\) and \(M_\infty\) represent the mass of water at time \(t\) and at equilibrium, respectively \(^{103, 104}\).

\[
\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-\frac{D(2n+1)^2 \pi^2 t}{4L^2}} \quad \text{(Eq. 2)}
\]

The mass uptake is frequently plotted against the square root of exposure time, and the so called Fickean diffusion profile is initially linear with a well defined equilibrium level. In the presence of swelling, the diffusion has rather been found to be a linear function of time \(^{105, 106}\) and also fracturing of the material is common \(^{106}\). This method does however not provide any information about solution constituents accumulated at the interface of an organically coated metal. A free film can also swell freely, while an attached adhesive brings about restrictions in
motion. Depending on the polymer used, the water uptake will be greater in either a free or an attached film. An increased water uptake in a free film has been assigned to its lack of rigidity, which means that distortions due to water penetration occur much faster. A greater transport through an attached film, although restricted in swelling, has been explained by a higher degree of capillary diffusion and by the possibility of accumulation at the interface. A poor adhesion may result in a faster water transport along the interface.

The presence of an electrolyte affects the water activity and leads to a decreased water uptake as compared to deionised water. Different theories exist concerning the transport of electrolytes through polymer films, e.g. that negatively charged pore walls act as selectively permeable membranes towards cations, or that cations rather are impeded due to their electrostatic attraction to these pore walls. There is a close relationship between the electrolytic resistance and the protective ability of the coating. Localized areas of different types of conductive behaviour have also been identified within one single polymer film.

1.3.4. Failure modes of the metal / polymer interface

The penetration of water and electrolyte through a polymer allows the formation of a corrosive environment and is detrimental for the metal / polymer interface. Although strong hydrogen-bonding contributes to the adhesion of a polymer film to the metal surface, the adhesion is to a large extent due to weaker physical interactions such as van der Waals forces, which are easily replaced by more stable bonds formed between the oxide and water. Delamination may also occur as a result of a specific corrosion process. One common mechanism for loss of coating adhesion on aluminium is anodic undermining, where loss of adhesion is obtained at low pH through anodic dissolution of aluminium or the aluminium oxide film. Anodic undermining is also suggested to be the most probable mechanism for filiform corrosion on coated aluminium. Cathodic delamination is a common failure mode of coated steel and zinc and is caused by alkalinity at the interface as a result of cathodic activity underneath the coating. If the transport of water along the interface is hindered by corrosion product formation, or by strong adhesive bonds, localized blistering will occur rather than delamination. Cathodic blister formation occurs in alkaline environments and in the vicinity of defects or conductive pathways, while anodic blistering demands a low pH to proceed. Osmotic phenomena such as osmotic blister formation and accumulation of water at the interface may also result from the presence of corrosion products at the metal surface and from hydrophilic material present due to contamination. Additionally, interfacial water along the interface can mechanically affect the blistered or delaminated film.

Apart from promoting corrosion and deterioration at the metal / polymer interface, the penetrating medium may also cause alterations of the polymer film itself. Phenomena such as plasticization and swelling may be reversible, but may also lead to irreversible processes such as cracking, crazing or hydrolysis. The polymer can also be subjected to degradation by aggressive reaction products. With a proceeding polymer breakdown, regions of electrolytic conductivity will exist randomly over the surface. Paths of complete penetration allow the electrolyte to meet the metal oxide interface and a corrosion cell is activated.
1.4. ATR-FTIR Kretschmann – The main methodology

1.4.1. Background of ATR-FTIR

Fourier transform infrared spectroscopy (FTIR) monitors the interaction between an electromagnetic field and a molecule as it undergoes a net change in dipole moment as a result of a vibrational or rotational motion. Molecular species that may obtain such a net change in dipolar moment will absorb infrared radiation at a frequency that exactly matches a frequency of molecular motion. When analysing an organic film, the technique may distinguish between the organic compounds and solutes within the film and measure the chemical interactions through shifts in band-positions in the IR spectrum. FTIR can be employed in different modes, but attenuated total reflection FTIR (ATR-FTIR) has the advantage of being applicable to thick films and opaque solutions. ATR-FTIR is based on total reflection of the incident IR radiation at the surface of an internal reflection element (IRE). Total reflection occurs for angles of incidence of the radiation greater than a certain critical angle, $\theta_c$, which is determined by Snell’s law (Eq. 3),

$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right) \quad \text{(Eq. 3)}$$

where $n_1$ and $n_2$ are the refractive indices of the IRE and of the sample, respectively. At the point of incidence, incoming and reflected radiation are superimposed to form a standing wave perpendicular to the surface of the denser medium, all in accordance with the field-matching boundary conditions imposed by the Maxwell equations. The amplitude and phase change of this electromagnetic standing wave will depend on the direction of the electrical vector of the wave front. This is divided into two components in the incident plane, one tangential to the surface and one normal to the incident plane. When polarized radiation is used, the perpendicular polarized radiation only obtains a tangential component ($E_y$). The light polarized parallel to the plane of incidence becomes elliptically polarized at the surface and obtains electric field components both tangential ($E_x$) and normal ($E_z$) to the surface. In the case of total reflection there is no net flow of energy transmitted across the IRE surface. However, a requirement for the standing wave, in order to fulfil certain boundary conditions in accordance with the Fresnel equations, is that the periodicity of the electromagnetic field in time and space is equal at both sides of the IRE surface. While the two tangential components, $E_x$ and $E_y$, are continuous across the IRE surface, the normal component, $E_z$, shows a discontinuity. For fulfilling of the boundary conditions, this $E_z$ component will experience a magnification of its electric field strength at the interface, a so called “field-matching.” This results in an evanescent field that passes into any optically less dense medium held in contact with the IRE. This evanescent field, with vector components in all spatial directions, holds an electric field amplitude, $E_0$, that decays exponentially with increasing distance from the IRE surface. Figure 1.4 shows a schematic picture of the set-up described, with $\theta$ as the angle of incidence of the incoming infrared radiation, $n_1$ as the refractive index of the IRE and $n_2$ as the refractive index of the optically less dense medium.
Figure 1.4. The standing wave amplitude characteristics in the vicinity of a totally reflecting interface, with the sinusoidal electric field amplitude in the IRE, $n_1$, and the exponentially decaying amplitude in the optically less dense medium, $n_2$.

When the optically less dense medium possesses an absorbing character and holds a complex refraction index $\bar{n} = n - i\cdot k$, where $k$ is the attenuation index, the evanescent field will be accompanied by an irreversible loss of energy. This means that the total internally reflected radiation is attenuated (reduced), while it results in a characteristic spectrum of the absorbing medium.

According to Harrick \(^{33}\), the depth of penetration, $d_p$, of this evanescent field is defined as the distance from the IRE where the electric field amplitude has decreased to $1/e$ of its value at the surface. For a non-absorbing interface, $d_p$ can be calculated according to Eq. 4,

$$
d_p = \frac{\lambda}{2\pi n_1 \left( \sin^2 \theta - \left( \frac{n_2}{n_1} \right)^2 \right)^{0.5}} \quad \text{(Eq. 4)}
$$

where $\lambda$ is the wavelength of the radiation \(^{33}\). This wavelength-dependence means that absorption bands at longer wavelengths (shorter wavenumbers) are relatively more intense than those at shorter wavelengths (higher wavenumbers).

If the IRE is coated with a polymer film prior to exposure to a penetrant, then any medium transported through the film will interact with the evanescent field within its depth of penetration and the components that are subjected to a change in its dipole moment will be detected. For a ZnSe element ($n_1 = 2.42$) covered with a polymer film and radiation incident at $75^\circ$, and by assuming the polymer and the penetrant medium to have a constant refraction index of $n_2 = 1.5$, the value of $d_p$ within the spectral region of interest would range from $\sim 0.2$ to $1.4$ µm (4000-600 cm\(^{-1}\)).
The effective thickness, $d_e$, is on the other hand defined as the actual strength of interaction of the evanescent wave with the sample, and represents the actual sample thickness that would be required to obtain the same absorption in a conventional FTIR transmission spectrum. For small absorptions, the value of $d_e$ may be approximated as described in Eq. 5 with the parameters defined according to Figure 1.4.

$$
d_e = \frac{n_2}{n_1 \cos \theta} \int_0^\infty E^2 dz = \frac{n_2}{n_1 \cos \theta} \int E_0 \cdot e^{-\frac{i}{\lambda_p}} dz \quad (\text{Eq. 5})
$$

This means that $d_e$ depends on the depth of penetration, $d_p$, the angle of incident radiation, and the refractive indices of the materials, as well as on the electric field strength, $E_0$, in the rare medium. When the thickness of the second medium is much greater than $d_p$, the value of $d_e$ is calculated according to Eq. 6.

$$
d_e = \frac{n_2}{n_1 \cos \theta} \int_0^\infty E^2 dz = \frac{n_2}{n_1 \cos \theta} \frac{E_0 \mu}{2 \cos \theta} \quad (\text{Eq. 6})
$$

As the imaginary refractive index still is assumed to be zero, also these equations are based on non-absorbing media. This type of ATR-FTIR investigations have been performed on the transport of water and other species through a polymer film to substrates made from various IRE-materials. The use of an infrared active ion has also made it possible to detect ionic species at the IRE / polymer interface. The analyses also provide valuable information regarding time-dependence and mechanisms of transport processes.
In order to obtain time-resolved diffusion data of relevance for an attached polymer film, the polymer can be coated directly onto the ZnSe IRE and exposed to the electrolyte. This makes it possible to extract the diffusion coefficient of water, \( D \), using the relation between Fick’s first law of diffusion (Eq. 1)\(^{103}\) and the ATR-FTIR absorption intensity of the water vibration band with time as deduced by Fieldson and Barbari\(^{104}\). For a homogenous film with neglected swelling, this relation constitutes an analogue to Eq. 2 and can be simplified as:

\[
\frac{A_t}{A_\infty} = 1 - \frac{8}{d_p} \cdot \frac{e^{-Dx^2t}}{2L} \cdot \left( \frac{\pi}{2L} \cdot e^{\left(-\frac{2L}{d_p}\right)} + \frac{2}{d_p} \right) \tag{Eq. 7}
\]

\( A_t \) and \( A_\infty \) are the absorbance at the time \( t \) and at saturation, \( L \) is the thickness of the polymer film, and \( d_p \) is the depth of penetration of the IR radiation as defined by Harrick\(^{33}\). This relationship is only valid for the polymer in direct contact with the IRE.

### 1.4.2. The ATR-FTIR Kretschmann geometry

While conventional ATR-FTIR analyses provide information about kinetics and mechanisms of transport processes, the results are not representative for more technically interesting surfaces such as metals. However, despite the strongly absorbing character of metals, an electric field can still pass through a thin metal film of tens of nanometers deposited onto an IRE. This is the so called ATR-FTIR Kretschmann geometry\(^{126}\). If the thin metal film is subsequently coated with a polymer film, the transport of species to the interface as well as changes in the metal / polymer interfacial region can be studied. Figure 1.6 shows a schematic picture of the set-up used for the surface-near analysis of the hidden interface between an aluminium film and a polymer.

\[\text{Polymer} \quad \text{ZnSe} \quad \text{Metal} \quad \text{Penetrating media} \]

\[\text{Hidden interface} \]

**Figure 1.6.** The hidden interface between an aluminium surface and a polymer film upon exposure to penetrating media.
As previously mentioned, the equations for extracting \(d_p\) and \(d_e\) (Eqs. 4 and 6) are based on non-absorbing media and can not be used for the systems including a thin metal film. While the resulting magnitude of the absorption bands is strongly related to the thickness and optical properties of the absorbing metal film applied to the IRE, the value of \(d_p\) (Eq. 4) is actually independent of the field strength; hence of the presence of a strongly absorbing metal film\(^{127, 128}\). The electric field amplitude value at the metal surface (\(E_0,\text{Metal}\)) will however be different from its value at the surface of a pure IRE (\(E_0\)), and will vary depending on the metal film-thickness. This means that there exists a practical limit in how thick the metal film may be while still allowing analysis with the ATR-FTIR Kretschmann geometry within the detection limits (Figure 1.7).

![Figure 1.7](image)

*Figure 1.7. (a) The ATR-FTIR set-up with an estimated depth of penetration and (b) the corresponding set-up of the ATR-FTIR Kretschmann geometry.*

Some authors\(^{118}\) have suggested an estimation of \(d_e\) for the case of an absorbing second medium by deriving a value of \(d_p\) (Eq. 4) with the imaginary parts of the refractive index included in the equation. This however results in a rather rough approximation of the physical process, with a different definition of \(d_e\) which now becomes dependant on concentration\(^{118}\). This kind of calculation is not employed in the present study, where ATR-FTIR Kretschmann is used as the main analytical tool for studies of the metal / polymer interfacial region upon exposure to corrosive conditions. Some corrosion-related studies have previously been performed by other authors using this technique, for example electrochemical reactions on iron\(^{129}\). On the other hand, studies of metal / polymer systems are more rare. Some authors detected water at different iron / polymer interfaces\(^{14, 105, 130, 131}\) and also corrosion was observed\(^{130}\).

In order to support data interpretation, calculated spectra may be derived from the Fresnel equations\(^{116}\), based on optical constants of each material as a function of the wavenumber and on the phase shift of the electrical field as it crosses each interface\(^{116, 132, 133}\). The reflected and transmitted light intensities for e.g. p-polarised radiation can be calculated at each interface using the matrix method for a stratified medium assuming plane parallel layers of homogeneous media with known refractive indices. The calculated reflection and transmission coefficients relate the electrical field strengths at each interface to the actual reflectance and transmittance of the whole stratified system. For instance, a program has
previously been developed at Swerea KIMAB AB that can be used for simulations of both IRRAS and ATR-FTIR Kretschmann spectra\textsuperscript{133}.

The dependence on the resulting IR absorption intensity of the metal film-thickness was investigated for the ATR-FTIR Kretschmann set-up by using thin films of gold exposed to de-ionised water. As gold is an inert metal, it can be concluded that all contributions to the IR spectrum are from water molecules only. Figure 1.8 displays the ATR-FTIR Kretschmann spectrum of water in contact with a gold-coated ZnSe IRE, together with the ATR-FTIR spectrum of water in contact with pure ZnSe\textsuperscript{133}.

![Figure 1.8. FTIR spectra of water on (a) gold-coated ZnSe (20 nm) and (b) pure ZnSe.](image)

Figure 1.8. FTIR spectra of water on (a) gold-coated ZnSe (20 nm) and (b) pure ZnSe.

Figure 1.9 shows the water peak intensity at 3370 cm\textsuperscript{-1} as a function of the gold film-thickness, based on both experimental data and data derived from calculated spectra.

![Figure 1.9. Water peak intensity at 3370 cm\textsuperscript{-1} as a function of the gold film-thickness on ZnSe: experimental data (···) and calculated data (—).](image)
As previously mentioned, thin metal films made from vacuum deposition have densities and optical and electrical properties that significantly differ from those of the bulk metal. These films may more resemble an array of dispersed islands. This means that information about the real and imaginary parts of the film dielectric constant and about the energy loss function are required for an accurate interpretation of the structural features.

In the presence of a metal film with a thickness below ~10-20 nm, an enhanced signal-strength of the ATR-FTIR absorption bands has been reported by several authors. This phenomenon was initially observed by Hartstein et al. for evaporated over- and underlayers of silver and gold, and has been referred to as surface enhanced ATR (SEIRA-ATR). The dominant factor for this enhancement effect is believed to be an enhanced localized electromagnetic field developed around the small particles that comprise the thin metal films. Contributions to the enhanced field are also likely to occur from chemical effects, such as charge-transfer interactions between adsorbate and metal. While the metal thicknesses used in the present work probably exceed the thickness of relevance for these phenomena, it should however be mentioned that such effects are not accounted for in the mathematically simulated spectra.

1.4.3. Integrated in situ ATR-FTIR Kretschmann and EIS

In this work, a spectro-electrochemical set-up was introduced that enables in situ ATR-FTIR Kretschmann measurements of polymer-coated metal substrates in combination with electrical impedance spectroscopy (EIS).

Spectro-electrochemical ATR-FTIR in the Kretschman geometry has previously been performed on uncoated metal surfaces for studies of adsorption and film formation under controlled potential. Nguyen et. al also studied water transport to an iron / polymer interface under potentiostatic conditions. To the author’s knowledge, no studies on polymer-coated metals have simultaneously combined any in situ FTIR technique with electrochemical impedance measurements. Recently, Vlasak et. al. however presented a study using combined ATR-FTIR and EIS for a polymer-coated semiconducting IRE made from silicon.

EIS is a conventional AC technique, commonly used for in-situ monitoring of water transport in attached polymer films on metal and constitutes a powerful tool for investigating deterioration and corrosion. The basis for determining water uptake by EIS is by modelling of the polymer film as the dielectric part of a capacitor. The impedance, Z, is used to measure the system capacity to resist the flow of an alternating electrical current. Compared to DC-techniques, EIS uses very small signals which do not disturb the electrode properties measured, and it is possible to use low conductivity media.

A physical model of the investigated process may be described by an equivalent circuit of electrical elements (resistors and capacitors) and other elements representing transport phenomena. Figure 1.10(a) displays the electrochemical response of an intact polymer film in contact with an electrolyte. This may be described as a purely capacitive element of the polymer (C_p) in series with an electrolytic resistance of the solution (R_E). Figure 1.10(b) shows the electrochemical response of a metal coated with a permeable film. When a resistive part (R_p) is introduced within the polymer film, any resulting process at the metal surface must be taken into account and the circuit has to be extended. The element B may for instance
symbolize a double-layer capacitance at the electrode surface, or a charge transfer resistance involved in for example a corrosion reaction, or a diffusion element for situations were the electrochemical reaction is limited by material transport \(^9, 10, 145\).

![Figure 1.10](image)

**Figure 1.10. Schematic electrochemical characteristics of a polymer-coated metal with (a) an intact film and (b) a permeable film. The electrical circuits constitute a reference electrode (RE) and a working electrode (WE).**

The measured response may be transformed from a time function into the frequency domain using Laplace transformations. The electrochemical response displayed as impedance relationships may then be presented as Bode plots with either the modulus of impedance, \( |Z| \), or the phase angle, defined as \( \tan \delta = Z''/ Z' \), versus log frequency. The frequency-dependence of the phase angle accounts for the time shift between the current and voltage sine waves and clearly indicates the presence of different time constants \(^9\). The results may also be displayed as a Nyquist plot, with the real impedance versus the imaginary impedance in the complex plane (Figure 1.11). Data interpretation can be performed by fitting of the impedance data to an equivalent electrical circuit, but often more than one circuit exist to describe the same response. This makes it difficult to interpret the response in terms of chemical and physical parameters \(^115\). Due to the overlapping of time constants it is very difficult to derive a transfer function of the reaction mechanisms for polymer coated metals.
Figure 1.11. Schematic electrochemical response of a polymer-coated metal displayed as Bode impedance, Bode phase angle and Nyquist plots for (a) an intact polymer film and (b) a permeable film with (I) and without (II) ongoing surface reactions.

Dipolar properties can be studied at high frequencies, while bulk properties generally can be studied at intermediate frequencies and surface properties at low frequencies. However, at longer exposure times these assumptions are not valid. For a polymer-coated metal, the properties of the polymer film at shorter exposure times can often be associated with the frequency region $10^3 - 10^5$ Hz, while the frequency region $< 1$ Hz provides information on interfacial changes.

During the initial part of the exposure, the water content in an intact polymer film can be estimated from impedance data by assuming the system to act as a purely plane-parallel capacitor, thus with the modulus of impedance proportional to the coating capacitance at the time $t$, $C_p(t)$.
\[ C_p(t) = \frac{\varepsilon \cdot \varepsilon_0 \cdot A}{L} \]  
(Eq. 8)

where \( \varepsilon \) is the relative dielectric constant, \( \varepsilon_0 \) is the dielectric permittivity of vacuum, \( A \) is the sample area and \( L \) is the coating thickness. By assuming a uniform water distribution in the polymer film and no polymer swelling (Fickean diffusion process), the diffusion of water can be translated to a water volume fraction, \( \phi \), using the mixing rule of Brasher and Kingsbury (Eq. 9), where \( \varepsilon_w \) is the dielectric constant of water at 20 °C and is set to 80

\[ \phi(t) = \frac{\log \left( \frac{C_p(t)}{C_p(t_0)} \right)}{\log \varepsilon_w} \]  
(Eq. 9)

At short exposure times, before contributions from surface processes become relevant, the diffusion coefficient for a polymer coating applied to a substrate may be estimated from the reduced water volume fraction, \( \phi(t)/\phi(t_\infty) \) (Eq. 10), where \( C_\infty \) is the capacitance at saturation

\[ \frac{\phi(t_0)}{\phi(t_\infty)} = \frac{C(t) - C(t_0)}{C(t_\infty) - C(t_0)} = \frac{4}{(2 \cdot L)} \sqrt{\frac{D \cdot t}{\pi}} \]  
(Eq. 10)
Figure 1.12 displays the experimental set-up based on combined ATR-FTIR Kretschmann and EIS.

Figure 1.12. Schematic view of the exposure cell for combined ATR-FTIR Kretschmann and EIS.
2. Experimental

2.1. Materials and sample preparation

Thin metal films were deposited onto IRE hemispheres made from ZnSe (Harrick Scientific Products Inc.) by high-vacuum evaporation of aluminium (99.9% pure, Ernest F. Fullam Inc.), zinc (99.9 % pure, Goodfellow) and gold (99.95 % pure, Goodfellow). The vacuum evaporators used were a JEE-4X/B (JEOL Ltd) (Papers I-III) and a Univex 300 (Leybold Vacuum) (Papers IV-VI), respectively. The aluminium film thicknesses were determined by inductively coupled plasma - atomic absorption spectrometry after dissolving the aluminium in a weak solution of hydrochloric acid (performed by ALS Laboratory Group, Luleå, Sweden). Evaporations performed by the Univex 300 were performed at an initial vacuum of $< 2 \times 10^{-5}$ mbar, and allowed an estimation of the metal film thickness using an in situ quartz crystal microbalance. The films produced by the older JEE-4X/B may have been of a higher porosity and higher oxide content, thus possibly allowing a higher absorption intensity compared to the thickness applied. The ZnSe IRE hemispheres were regenerated by dissolving the aluminium and zinc in weak HCl and dissolving the plain polymer films in dichloromethane. The gold and structural polymer coatings were removed by grinding and polishing to a surface roughness of ~1 µm.

In Papers I-III the simple model systems used were all manually casted onto the metal-coated ZnSe IRE. The polymers used were a transparent, one component, adhesive based on nitrile rubber and a vinylchloride-vinylacetate co-polymer (Bostik 1782, Bostik Findley AB), a transparent alkyd varnish (Syntoflex Klarlack, Becker Industrifärg AB), a pigmented two-component epoxy adhesive (Auto marine epoxy +300, JB Weld) and a pigmented acrylic-based sealant (Rubson Easy Fix, Henkel), respectively.

In Papers IV-VI, a pre-treatment was applied to the metal-coated IRE prior to coating with a polymer. In Paper IV, the evaporated zinc surface was converted by spray application of a 10% (pH 3) aqueous solution based on hexafluorotitanic acid, manganese salts, phosphoric acid and organic components (Henkel KGaA). A titanium content of 8-18 mg/m² was verified by X-ray fluorescence (performed at Högskolan Dalarna, Sweden). A UV-curing polymer film, based on a modified epoxy acrylate, was cast manually on top of the zinc conversion layer and was cured under an Oriel UV-lamp at 0.55 J/cm². In Papers V and VI a water-based silane mixture was used based on pre-hydrolysed γ-aminopropylsilane (γ-APS) and bis[3-triethoxysilylpropyl]ethane (BTSE) (Chemetall GmbH) (Figure 2.1).

![Figure 2.1. The chemical formulae of pre-hydrolysed (a) γ-APS and (b) BTSE.](image)

In order to promote the hydrolysis of BTSE and prevent pre-condensation reactions, the silane system was purchased pH-adjusted with acetic acid. The deposition of silane was performed
on thin films of aluminium and gold, respectively. Prior to application of the silane, the aluminium surfaces were subjected to one minute of alkali-cleaning in pure NaOH of pH 10.5 (Merck KGaA) using an application cell made for the ZnSe crystal substrates (Figure 2.2), followed by thorough rinsing in distilled water and drying with compressed air.

The silane mixture was applied horizontally to an area of ~ 2.3 cm$^2$ from a 2 wt% solution and baking took place at 90 °C for one hour. The transparent one-component epoxy top-coat, based on bisphenol-A and a urea resin cross linker (Beckers Industrial coatings), was applied by spin coating and cured at 180 °C for 20 minutes.

The samples were exposed either to ultra-pure deionized water (Purelab UHQ, ELGA), to a 1 M sodium thiocyanate (NaSCN) solution (purum, Sigma Aldrich) dissolved in ultra-pure deionised water, or to a 0.1 M sodium chloride solution (BDH AnalaR). The reason for sometimes using a thiocyanate solution as model electrolyte, instead of a more technically interesting chloride solution, is that chloride is non-active in the infrared region and cannot be detected. The thiocyanate ion is a polyatomic pseudo-halide ion which resembles the halide ion in its chemical properties$^{118}$.

2.2. Experimental techniques

2.2.1. ATR-FTIR Kretschmann

The ATR-FTIR Kretschmann analyses were performed using a Bio Rad FTS 175C or a Varian 7000 spectrometer equipped with a DTGS detector and a Harrick Seagull$^{\text{TM}}$ multi-purpose reflection attachment. The measurements were performed using p-polarized radiation (KRS-5 or ZnSe wire grid polarisers) and IR radiation incident at 65° or 75°. The spectra were obtained in the region of 4500-600 cm$^{-1}$, using a resolution of 16 cm$^{-1}$ and between 56 and 4000 scans. The same parameters were also employed for the ATR-FTIR analyses performed on the pure ZnSe IRE hemispheres. All spectra are presented in the absorbance form, $-\log(R/R_0)$, where R is the reflectance of the sample and $R_0$ is the reflectance of the background.
The in situ ATR-FTIR Kretschmann analyses upon exposure to electrolyte were performed in an exposure cell holding ~0.5 cm$^3$ sealed with a rubber gasket. The temperature of the sample was 29 ±1 °C due to heating by the infrared radiation. The background spectra were recorded from the dry sample prior to exposure, after which the exposure medium was injected into the sample cell using a syringe while temporarily removing the cell from the sample compartment.

The ATR-FTIR Kretschmann studies combined with EIS were all performed using the Varian 7000 spectrometer. In order to fit in the electrochemical tools, enlarged exposure cells were constructed from poly(ether-ether-ketone) with connections for the reference electrode and the counter electrode, respectively. The exposure cells, holding ~10-15 cm$^3$ of exposure media, were sealed to the sample with a rubber gasket. For the electrical connection to the working electrode, an aluminium wire was attached to the working electrode by a conductive epoxy adhesive (Chemtronics). The exposure medium was injected with the cell still remaining in the sample compartment after recording of the background spectrum.

### 2.2.2. EIS

The EIS measurements were performed using an Autolab PGSTAT 302 potentiostat with an FRA2 frequency response analyzer (Eco Chemie B.V.). A sinusoidal AC perturbation of 15 (Papers II-IV) or 40 (Paper VI) mV amplitude and open circuit potential was applied to the 1.1 cm$^2$ working area. Data were collected between 10$^5$ and 10$^{-2}$ Hz, with 10 points/decade, and a current range between 10$^{-2}$ and 10$^{-7}$ A. The set-up used either an Ag/AgCl REF321 XR300 reference electrode (Radiometer Analytical SAS) with a luggin capillary and an M241Pt Platinum counter electrode (Radiometer Analytical SAS) (Papers II-IV) or an Ag/AgCl REF321 XR300 reference electrode directly into the exposure chamber and pure Pt as counter electrode (Paper VI). The results were presented as Bode plots with both the modulus of impedance and the phase angle versus log frequency, and as Nyquist plots with the real impedance versus the imaginary impedance.

### 2.2.3. IRRAS

The IRRAS analyses were performed using a Bio Rad FTS 175C or a Varian 7000 spectrometer equipped with a DTGS detector and a Harrick Seagull$^\text{TM}$ multi-purpose reflection attachment. The measurements were performed using p-polarized radiation (KRS-5 or ZnSe wire grid polarisers) and IR radiation incident at 75 or 78°. The spectra were obtained in the spectral region of 4500 - 400 cm$^{-1}$, using a resolution of 8 cm$^{-1}$, and with the background spectrum recorded on the dry untreated sample.
2.2.4. Complementary FTIR analyses

Additional characterisations were performed by FTIR transmission spectroscopy using a Bio Rad FTS 175C and conventional ATR-FTIR analyses were conducted using a Harrick SplitPea™ attachment equipped with a Si crystal.

2.2.5. EDX

The thickness of the silane film (Papers V and VI) was measured on an aluminium sheet by energy dispersive x-ray spectroscopy (EDX) which was performed with a field emission gun scanning electron microscope (FEG-SEM) Leo1530, upgraded to correspond to the Zeiss Supra 55 and equipped with the EDX and connected to an INCA system from Oxford Instruments. The cross-section analysis was performed using 15 kV and a magnification of 3000x.

2.2.6. GDOES

Surface film analyses (Papers IV and V) were performed using glow discharge optical emission spectroscopy (GDOES) with a LECO GDS 750A (LECO Technik GmbH).

2.2.7. Gravimetrical measurements

Thin adhesive films were exposed at 25 °C to ultra pure deionised water, to 1 M NaSCN (Paper III) and to 1 M NaCl (Paper VI), respectively, and were continuously weighed on a micro-balance (Sartorius MC210P, 0.05 mg readability).
3. Results and discussion

3.1. Initial studies by in-situ ATR-FTIR Kretschmann

As a pre-study before the investigation on polymer-coated metal, the pure ZnSe IRE and ZnSe coated with a thin aluminium film were investigated upon exposure to deionised water and to an electrolyte (1 M NaSCN), respectively. The resulting ATR-FTIR Kretschmann absorption spectra are displayed in Figure 3.1.

Upon exposure to water (Figure 3.1a), both IR-spectra show a broad and strong band between 3700 and 3000 cm\(^{-1}\). For water in contact with the pure ZnSe surface, this band may be assigned to symmetric and asymmetric stretching vibrations of water molecules, but on the aluminium surface contributions also arise from hydroxyl (-OH) stretching vibrations due to aluminium hydroxide formation\(^{42,148-150}\). Different types of interactions may exist between water and the ZnSe surface compared to between water and the oxidised aluminium. In contact with the pure ZnSe element, water molecules only exist as bulk-like water, possibly with a more ordered structure in the vicinity of the surface. On the aluminium-coated ZnSe element, water may however also exist in smaller aggregates as incorporated within a porous aluminium oxide/hydroxide film developed on the aluminium surface. The water-spectrum on aluminium-coated ZnSe shows a band maximum at 3450 cm\(^{-1}\), while water in contact with the pure ZnSe shows a band maximum at 3370 cm\(^{-1}\) and a pronounced shoulder at ~3240 cm\(^{-1}\). An additional broad band is obtained at ~2100 cm\(^{-1}\) assigned to a combination of the bending vibrations and librations of bulk water\(^{151}\). The narrow peak observed in both spectra between 1700 and 1500 cm\(^{-1}\), with a maximum at ~1650 cm\(^{-1}\), is due to the H-O-H bending vibrations of the water molecule. In all spectra, librations (frustrated rotations) of liquid water contribute
to the band below \( \sim 1000 \text{ cm}^{-1} \). In the presence of an aluminium film an additional band appears between 1100 and 900 cm\(^{-1}\), with a maximum at \( \sim 950 \text{ cm}^{-1} \), assigned to stretching vibrations of Al-O \(^{149}\) and/or to bending vibrations of Al-OH \(^{148}\) due to oxidation and hydration reactions of the aluminium surface. The spectra obtained upon exposure to the electrolyte (Figure 3.1b) are similar to the corresponding exposure to water, but a narrow peak is observed between 2120 and 2040 cm\(^{-1}\) with a maximum at \( \sim 2070 \text{ cm}^{-1} \). This peak is assigned to cumulated C=N stretching vibrations of the thiocyanate species (S=C=N) \(^{152, 153}\). The weak shoulder at 2110 cm\(^{-1}\) observed in the presence of the thin aluminium film implies a specific interaction with the aluminium surface that does not occur on the ZnSe surface. This means that the peak at 2070 cm\(^{-1}\) is due to thiocyanate ions in the electrolyte solution while the shoulder at 2110 cm\(^{-1}\) can be assigned to ionic species that are either specifically adsorbed on the oxidised aluminium surface or become incorporated within the thin surface film \(^{141, 154, 155}\).

These results show that water and ionic species can be detected and characterised at the surface of a metal-coated IRE. The band positions are strongly related to the optical properties of the IRE \(^{156}\), which may be a major reason for a divergence in band position obtained when a metal film is applied to an IRE. Additionally, the different effective depth of analysis from the two substrates is likely to result in different proportions of the various water types detected.

### 3.2. In situ ATR-FTIR Kretschmann studies

In order to study changes at a hidden metal / polymer interface, aluminium-coated ZnSe with a simple polymer top-coat were exposed to corrosive media. The results are presented in detail in Paper I. First, the hidden aluminium / polymer interface was studied in contact with deionised water, using aluminium-coated ZnSe with a polymer film on top. An adhesive based on nitrile rubber and a vinylchloride-vinylacetate co-polymer (~25-50 µm thick) was used as a model polymer system. Figure 3.2 shows selected ATR-FTIR Kretschmann spectra along with the absorption intensity of certain band maxima as a function of time.

![Figure 3.2](image-url). (a) ATR-FTIR Kretschmann spectra of a aluminium-coated ZnSe element with an adhesive film after 0.75, 3, 26 and 50 hours of exposure to ultra-pure deionised water, and (b) the corresponding absorption intensity at 3450, 1650 and 960 cm\(^{-1}\) versus the exposure time.
Within 40 minutes of exposure, a broad and strong band was observed at ~3450 cm\(^{-1}\) due to stretching vibrations of water molecules and of hydroxyl (-OH) groups from any formation of aluminium hydroxide at the surface. Additional bands appear at ~1650 cm\(^{-1}\), assigned to H-O-H bending vibrations of water molecules, and below 1100 cm\(^{-1}\) assigned to librations of liquid/bulk water. With time, a relatively sharp absorption band appears at ~1050-850 cm\(^{-1}\), with a maximum at ~960 cm\(^{-1}\), assigned to aluminium oxidation and hydration reaction products.

The absorption intensities of the peak maxima at 3450, 1650 and 960 cm\(^{-1}\) as a function of exposure time show different behaviours. Figure 3.2b shows a rapid initial increase of the hydroxyl (–OH) band at 3450 cm\(^{-1}\), but a corresponding slow increase of the peak at 960 cm\(^{-1}\) assigned to Al-O vibrations. This indicates a water uptake into the polymer network with only limited contributions from oxidation and hydration processes of the aluminium surface. The water transport through a polymer film of limited swelling is expected to level out after longer times of exposure. The lack of constant absorption level for the absorbance band at 1650 cm\(^{-1}\) during this exposure means that water molecules keep entering the interfacial region. After penetrating the polymer film, water molecules may exist either in the form of a water film at the aluminium / polymer interface, as microscopic water-filled cavities (clusters), or as water aggregates incorporated within the surface-near polymer network or the porous aluminium oxide/hydroxide film. Additional studies showed that the presence of water within this porous aluminium oxide/hydroxide film is limited (see Paper I). This implies that water is continuously incorporated within the polymer network.

Next was considered the transport of electrolyte to the aluminium / polymer interfacial region and its interactions at the aluminium surface. Figure 3.3 shows some ATR-FTIR Kretschmann spectra along with the absorption intensity of certain band maxima as a function of time.
Figure 3.3. (a) ATR-FTIR Kretschmann spectra of a ZnSe element coated with a thin aluminium film and an adhesive film after 0.75, 4, 23 and 47 hours of exposure to 1 M NaSCN and (b) the corresponding absorption intensity at 3450, 1650 and 2075 cm$^{-1}$ versus the exposure time.

At short exposure times, the qualitative results are in agreement with the exposure in deionised water (Figure 3.2a), with stretching vibration bands of water molecules and hydroxides (3700-3000 cm$^{-1}$), bending vibrations of water (1650 cm$^{-1}$), and various water and Al-O / Al-OH vibrations (below ~1100 cm$^{-1}$) observed in the IR spectra. After around 10 hours of exposure, a narrow peak is observed at ~2075 cm$^{-1}$ assigned to cumulated C=N stretching vibrations of the thiocyanate species that constitute the electrolyte. While the water sorption profile at 1650 cm$^{-1}$ shows a fast initial increase and reaches its maximum level within five hours of exposure, the band assigned to thiocyanate at 2075 cm$^{-1}$ increases linearly with time. This indicates that thiocyanate species move within the polymer network with a different transport mechanism than water, and are accumulated at the interface within the surface-near polymer network or within corrosion products formed at the aluminium surface. The constant absorption level reached for both water-related bands is in contrast to the exposure to ultra pure deionised water (Figure 3.2b) and indicates a repressed water ingress caused by a smaller osmotic pressure gradient obtained in the presence of an electrolyte.
To summarise, in situ ATR-FTIR in the Kretschmann geometry allowed studies of the hidden interfacial region between an aluminium surface and a polymer film during exposure to water and electrolyte. The technique provided valuable information regarding transport of water and infrared active ionic species to the metal surface, as well as of surface processes such as oxidation and hydration.

### 3.3. Integrated in situ ATR-FTIR Kretschmann and EIS

The processes at a hidden metal / polymer interface were further investigated by the extended set-up with in situ ATR-FTIR Kretschmann combined with EIS. First, the interactions at the hidden interface between pure aluminium and four different plain polymer systems were studied upon exposure to an electrolyte solution (Section 3.3.1). The results are described in detail in Papers II and III, respectively. Furthermore, the set-up was employed for determining the applicability of the technique for studies of hidden metal / polymer interfaces in the presence of a chemical pre-treatment (Section 3.3.2). The results are described in detail in Papers IV and V, respectively.

#### 3.3.1. Introductory examples using plain polymer-coated aluminium

The hidden interfaces between pure aluminium and four different polymer systems were studied upon exposure to an electrolyte solution. The first system consisted of aluminium-coated ZnSe coated with the same adhesive that was investigated in Section 3.2, but with a coating thickness of ~10-20 µm. The water diffusion coefficient of the polymer attached to a pure ZnSe element and exposed to 1 M NaSCN was estimated to $10^{-9}$ cm$^2$/s according to Eq. 7. The corresponding free polymer film obtained a maximum weight increase of ~2 wt% in the gravimetric testing. ATR-FTIR Kretschmann and EIS measurements were performed simultaneously during exposure to a 1 M NaSCN solution. The resulting IR spectra and Bode impedance plots obtained after certain times of exposure are presented in Figure 3.4, together with the IR absorption intensities of the peaks at 1650 and 2075 cm$^{-1}$ versus the exposure time.
Figure 3.4. (a) ATR-FTIR Kretschmann spectra and (b) EIS Bode impedance plots for aluminium-coated ZnSe further coated with an adhesive film after 0.25, 2, 10 and 55 hours of exposure to a 1M NaSCN solution, together with (c) the IR absorption intensity at 1650 and 2075 cm$^{-1}$ versus the exposure time.

In accordance with the previous results (Figure 3.3a), IR absorption bands are observed within 15 minutes of exposure at 3700-3000 cm$^{-1}$, at ~1650 cm$^{-1}$ and below 1000 cm$^{-1}$ assigned to the presence of water molecules in the aluminium / polymer interfacial region. In agreement with this, the modulus of impedance shows a plateau at low frequencies, which indicates the presence of electrolytic pathways all the way down to the aluminium surface$^{9, 89, 158}$. Up to 2 hours of exposure, a significant water uptake across the polymer film is observed and followed by the ATR-FTIR Kretschmann technique. The corresponding modulus of impedance shows a decrease at frequencies below ~10 Hz, with an additional time-constant developing below ~1 Hz$^9$. The weak IR band observed at ~1000 cm$^{-1}$ suggests that oxidation and hydration reactions of the aluminium surface still are of limited importance. This indicates that the EIS-response up to this point is due to partial delamination rather than to oxidation processes. Within around 2 hours of exposure, a band is observed at ~2075 cm$^{-1}$ assigned to the cumulative C=N stretching vibration of thiocyanate species. The time-dependence of the band intensity indicates an initial fast ingress due to a free electrolytic pathway, but this is followed by a constant growth rate more in agreement with the behaviour
observed for the somewhat thicker film (Figure 3.3b). While the water band at \( \sim 1650 \text{ cm}^{-1} \) reached a maximum value within \( \sim 10 \) hours of exposure, the C=N vibration at \( \sim 2075 \text{ cm}^{-1} \) continued to increase with time. This implies a different transport mechanism of water and thiocyanate species through the polymer bulk. After 10 hours of exposure, the modulus of impedance has decreased further at intermediate frequencies while the frequency region below \( \sim 1 \text{ Hz} \) has experienced an increase in impedance. This suggests a build-up of corrosion products that cover already delaminated areas or impede the passage of conducting species to the surface by blocking existing electrolytic pathways in the surface-near polymer network\(^{85,159}\). This hypothesis is supported by the IR band observed after around 5 hours of exposure at \( \sim 1000 \text{ cm}^{-1} \), assigned to Al-O and Al-OH vibrations of aluminium oxidation and hydration reaction-products at the aluminium surface. The maximum absorption level of the water band at \( \sim 1650 \text{ cm}^{-1} \) was reached within 10 hours of exposure. This suggests that the continuous increase of the –OH vibration band at \( \sim 3490 \text{ cm}^{-1} \) is assigned to ongoing formation of aluminium hydroxide at the surface. Also the position of the band maximum at \( \sim 3490 \text{ cm}^{-1} \) indicates a significant contribution of Al-OH. The peaks observed between 1600 and 1400 cm\(^{-1}\) are assigned to degradation products and/or to molecular rearrangements of the polymer network. These bands severely obstruct the shape of the band at \( \sim 1650 \text{ cm}^{-1} \) and make the absorption intensity of this band difficult to follow as a function of the exposure time.
The second system investigated consisted of aluminium-coated ZnSe further coated with a transparent alkyd varnish film (5-10 µm thick). The water diffusion coefficient of this polymer directly attached to a pure ZnSe element and exposed to 1 M NaSCN was in the order of ~10⁻¹⁰ cm²/s, which is a reasonable value for a polymer film that lacks large pores or defects. The corresponding free polymer film obtained a maximum weight increase of ~2 wt%. Figure 3.5 shows the ATR-FTIR Kretschmann spectra and EIS Bode impedance plots after certain times of exposure to the 1 M NaSCN solution, together with the IR absorption intensities of the peaks at 1650 and 2075 cm⁻¹ versus the exposure time.

Analogously with the previous results, IR bands are observed within 20 minutes of exposure assigned to OH-vibrations of water and aluminium hydroxide (3700-3000 cm⁻¹) and to molecular water (~1650 cm⁻¹). The modulus of impedance shows an initial plateau at low frequencies, which is characteristic of resistive properties and the presence of pores or small defects in the polymer film. After 20 minutes of exposure, the maximum of the -OH band is located at ~3500 cm⁻¹, which is indicative of a low degree of hydrogen bonding and weak

Figure 3.5. (a) ATR-FTIR Kretschmann spectra and (b) EIS Bode impedance plots for aluminium-coated ZnSe further coated with a transparent alkyd film after 0.3, 3, 6 (EIS only), 34 and 75 hours of exposure to 1 M NaSCN, together with (c) the IR absorption intensity at 1650 and 2075 cm⁻¹ versus the exposure time.
water molecular interactions. At short exposure times, a larger contribution to the position at higher wavenumbers may also arise from the presence of aluminium hydroxide vibrations (Al-OH). However, no signs of active corrosion or surface film formation can be deduced from either the IR spectra in the region of \( \sim 1000-900 \text{ cm}^{-1} \) or the EIS data \(^9,10\). After 3 hours of exposure an IR band observed at \( \sim 960 \text{ cm}^{-1} \) implies that the aluminium surface has become subjected to oxidation or hydration reactions due to the water ingress. Also thiocyanate species are detected at \( \sim 2075 \text{ cm}^{-1} \) as a result of water and electrolyte reaching the interface. The shift in maximum of the \( \sim \text{OH} \) band towards \( \sim 3460 \text{ cm}^{-1} \) would mainly be due to the formation of larger water aggregates. The modulus of impedance is further lowered as a result of an increased water uptake and after 6 hours of exposure a decrease is observed at frequencies up to \( 10^4 \text{ Hz} \). At this time, a new time-constant due to surface processes can be observed in the low-frequency region as a result of ongoing oxidation processes. Such an impedance-response could also result from a delamination process, without any significant corrosion attack. However, the IR band assigned to Al-O and Al-OH reaction products (960 \text{ cm}^{-1}) gradually increases in intensity up to 34 hours of exposure and verifies that corrosion is a major origin of this response. Up to this time, also the IR peaks at 1650 and 2075 \text{ cm}^{-1} assigned to water and thiocyanate species steadily increase, but with different time dependence. The linear increase of the C=N stretching vibration band at 2075 \text{ cm}^{-1} indicates that thiocyanate species are continuously transported through the alkyd varnish and are accumulated at the aluminium / alkyd interface. The absorption intensity at 1650 \text{ cm}^{-1} shows a significant deviation from Fickian-like behaviour, which probably results from polymer swelling as well as from partial loss of adhesion from the aluminium surface. After 34 hours of exposure, the modulus of impedance decreases in the whole frequency region and the absorption intensities at 1650 and 2075 \text{ cm}^{-1} experiences an abrupt increase. This is indicative of an onset of severe delamination, with a significant amount of electrolyte solution at the aluminium surface, and is also confirmed by the low impedance value and close to frequency-independent response in the high frequency region of the Bode plot obtained during prolonged exposure \(^{10}\). This means that the onset of significant delamination of the alkyd film from the aluminium surface can be observed by both ATR-FTIR Kretschmann and EIS. The peaks obtained at 1725, 1263, 1120 and 1070 \text{ cm}^{-1} after longer exposure times are all in agreement with the IR spectrum of the polymer and are assigned to degraded polymer material or to a water-induced molecular rearrangement.
The third system investigated consisted of aluminium-coated ZnSe with a pigmented epoxy top-coat (30-50 µm thick). The water diffusion coefficient of the epoxy film attached to a pure ZnSe element was estimated to ~10^{-10} cm^2/s, but with a maximum weight increase of ~ 4 wt% for free films. Figure 3.6 shows the ATR-FTIR Kretschmann spectra and Bode impedance plots after certain times of exposure to the 1M NaSCN solution, along with the absorption intensity of the peaks at 1650 and 2075 cm^{-1} versus the exposure time.

The initial plateau of the modulus of impedance observed at low frequencies in the Bode impedance plots indicates that the epoxy adhesive possesses resistive properties, with water/electrolyte entering the polymer network. Still, the IR spectrum indicates that no electrolyte constituents have yet reached the aluminium / epoxy interfacial region. After one
hour of exposure, only limited further changes are observed in the Bode impedance plot. This indicates that the epoxy adhesive film possesses resistive properties, with water/electrolyte entering the epoxy polymer network, but that the film is still protecting against active corrosion. As displayed in Figure 3.6c, a time-lag of ~7 hours is needed for water to reach the interfacial region, probably impeded by pigment particles that absorb the solution until saturation. After 11 hours of exposure, IR bands can be assigned to –OH functionalities (~3450 cm\(^{-1}\)), molecular water (~1650 and < 1100 cm\(^{-1}\)) and thiocyanate species (~2075 cm\(^{-1}\)) present at the aluminium / epoxy interface. The modulus of impedance at this point is significantly decreased in the whole frequency region, although the epoxy film still shows some protective capacity at high frequencies. A new time constant is observed at frequencies < 50 Hz, which indicates a separation between paint and substrate and could be associated with interfacial reactions and the formation of a layer of corrosion products at the aluminium / epoxy interface \(^9, 10\). Despite the strong overlap of IR bands assigned to water librations below 1100 cm\(^{-1}\), a narrower peak is observed at ~990 cm\(^{-1}\) assigned to various Al-O and Al-OH vibrations that supports the EIS interpretation of ongoing oxidation and hydration reactions at the aluminium surface. Between 11 and 41 hours of exposure, the modulus of impedance keeps decreasing, indicative of the formation of porous hydroxides rather than of a build-up of a more “protective” surface film. This is in agreement with the considerable growth of the broad band at 990 cm\(^{-1}\). The absorption intensities of both electrolyte constituents increase in time, but with different kinetics. This continuous transport indicates that few free pathways exist and that the transport mainly occurs through smaller pores or by segmental motion of the polymer network. Between 41 and 159 hours of exposure, a significant increase of the modulus of impedance is observed in the low-frequency region. This new capacitive behaviour suggests a significant corrosion formation that seals the delaminated surface and hinders the passage of conducting media to the surface \(^85, 159\). This is supported by the significant growth of the broad band at ~990 cm\(^{-1}\) assigned to aluminium oxidation products. While the IR absorption intensity of water at ~1650 cm\(^{-1}\) approaches a maximum level within 140 hours of exposure, the corresponding response from the thiocyanate-related band at ~2075 cm\(^{-1}\) is continuously increasing during the whole exposure, suggesting an accumulation of thiocyanate at the hidden interface. After longer exposure time, additional peaks are obtained at 1510 and 1420 cm\(^{-1}\) as a result from polymer degradation and molecular rearrangements.
The fourth system consisted of aluminium-coated ZnSe element further coated with a pigmented acrylic-based sealant (30-50 µm thick). The water diffusion coefficient of the pigmented acrylic based sealant attached to a pure ZnSe element was estimated to ~10^{-9} \text{cm}^{2}/\text{s}, while the maximum weight increase of the free polymer film was as high as ~30 wt%. Figure 3.7 presents the ATR-FTIR Kretschmann spectra and Bode impedance plots after certain times of exposure to a 1 M NaSCN solution, along with the absorption intensity versus the exposure time for the peaks at 1650 and 2075 cm^{-1}.

![Figure 3.7](image_url)

*Figure 3.7. (a) ATR-FTIR Kretschmann spectra and (b) EIS Bode impedance plots for aluminium-coated ZnSe further coated with a pigmented acrylic-based sealant after 0.25, 4.5, 10.5 and 12 hours of exposure to 1 M NaSCN, together with (c) the IR absorption intensity at 1650 and 2075 cm^{-1} versus the exposure time.*

The modulus of impedance shows an initial plateau at low frequencies which is assigned to a comparably large immediate water uptake. The IR spectra show similar qualitative features as the previously examined systems, with –OH stretching vibrations at 3700-3000 cm^{-1}, bending vibrations and librations of water at ~1650 cm^{-1} and ~<1000 cm^{-1}, respectively, and with a narrow peak at ~2075 cm^{-1} assigned to thiocyanate species. The peak observed between 1130 and 1020 cm^{-1} is assigned to Al-O and Al-OH vibrations of aluminium oxidation and...
hydration products. The position of the maximum at ~1085 cm\(^{-1}\) is however higher than for the corresponding aluminium oxidation bands previously observed (Figures 3.4-3.6). This implies that this surface film contains a more significant amount of Al-OH vibrations assigned to aluminium hydroxide or aluminium oxy-hydroxides compared to the other systems\(^{160}\). After 4.5 hours of exposure, the modulus of impedance has experienced a decrease at intermediate-to-high frequencies, but still with preserved capacitive behaviour at high frequencies. This indicates a considerable water uptake of the polymer network, and is in accordance with the negative absorption peaks observed in the IR spectra in the region of 3700-3000 cm\(^{-1}\) and below 1500 cm\(^{-1}\). These negative bands are assigned to a decreased polymer concentration in the surface-near region as a result of swelling or delamination of the polymer network. However, delamination is less plausible considering the EIS result observed. As the exposure proceeds, the modulus of impedance is further decreased in the whole frequency region as a result of ongoing surface processes. Additionally, a new time constant appears in the Bode plot below ~10 Hz in agreement with a build-up of corrosion products. Finally, the response in the high-frequency region after 12 hours of exposure shows the characteristic behaviour of a delaminated metal surface, with a frequency-independent character, and a significant amount of electrolyte present to separate the polymer film from the aluminium surface\(^{10}\). The time-dependence of the absorption peaks at 1650 and 2075 cm\(^{-1}\) shows similar character, which implies a joint transport of thiocyanate species and water at such a high level of uptake. As a result of significant swelling of the polymer network, no constant level of these bands is reached.

To summarise, the use of simultaneous ATR-FTIR Kretschmann and EIS was found to give consistent and complementary information from the hidden metal / polymer interfaces upon exposure to an electrolyte. The transport of water and electrolyte through the polymer films to the aluminium / polymer interface and the subsequent corrosion of the aluminium surface was followed by ATR-FTIR Kretschmann, while the protective properties of the polymer film were simultaneously studied by EIS. Despite similarities regarding water diffusion coefficient or maximum water uptake, the four different polymer systems investigated were found to show considerably different behaviours.

3.3.2. Polymer-coated metal including a chemical pre-treatment

The integrated in situ ATR-FTIR Kretschmann and EIS set-up was further employed in order to gain a deeper understanding of hidden metal / polymer interfaces where the metal surface has been treated with an environmentally friendly chemical pre-treatment. The results are described in detail in Papers IV-VI.

3.3.2.1. Titanium-based conversion of zinc

The hidden interface between a conversion-coated zinc surface and a polymer coating was investigated upon exposure to an electrolyte. The detailed results are presented in Paper IV. To provide a reference, the ATR-FTIR Kretschmann spectrum of a conversion-coated zinc surface on ZnSe is displayed in Figure 3.8, together with a GDOES surface depth-profile performed on a zinc sheet.
Figure 3.8. (a) ATR-FTIR Kretschmann spectra of conversion-coated zinc on ZnSe and (b) GDOES depth-profiling performed on a zinc sheet.

The surface depth profile shows major contributions from oxygen and phosphorous, with smaller amounts of titanium, manganese and carbon, and the layer thickness was roughly estimated to be around 100 nm. The IR band observed between 3700 and 2900 cm\(^{-1}\) is assigned to -OH stretching vibrations from the mixture of metal (Zn, Ti and Mn) oxides, hydroxides and phosphates of the conversion coating. The presence of a molecular water-band at ~1650 cm\(^{-1}\) indicates that the conversion layer incorporates some water, which in turn contributes to the broad -OH band with a maximum at ~3380 cm\(^{-1}\). The strong peak observed at ~1080 cm\(^{-1}\) is assigned to phosphate compounds from the conversion coating, but also various metal oxidation-products contribute in the spectral region below 1200 cm\(^{-1}\). The presence of organic components in the surface layer is manifested as minor peaks between 3000-2800 cm\(^{-1}\) and 1500-1200 cm\(^{-1}\).

Furthermore, the ATR-FTIR Kretschmann spectra obtained for pure zinc and for converted zinc, respectively, upon exposure to 1 M NaSCN are displayed in Figure 3.9.

Figure 3.9. The ATR-FTIR Kretschmann spectra of (a) pure zinc exposed for 8 and 13 minutes and (b) a converted zinc film exposed for 15 minutes and 2 hours to a 1 M NaSCN solution.
Figure 3.9a shows a broad band with a maximum at ~3400 cm$^{-1}$ assigned to -OH stretching vibrations. As the spectra lack bands assigned to Zn-OH bending vibrations$^{162}$, the major contribution to the –OH band is likely to originate from water. The bands observed at ~1650 cm$^{-1}$ and below 1000 cm$^{-1}$ are assigned to water bending vibrations and librations, respectively,$^{42}$ and the peak at ~2075 cm$^{-1}$ is due to the C=N stretching vibration of thiocyanate$^{152,153}$. The small bands observed at ~1330 cm$^{-1}$ and ~1520 cm$^{-1}$ are assigned to carbonates such as Zn$_5$(OH)$_6$(CO$_3$)$_2$$^{29}$, which is a frequent corrosion product on zinc at atmospheric conditions. Due to the cutting limit for the ZnSe IRE used, the Zn-O vibrations occur outside the wavenumber range investigated$^{30}$. Dissolution and thinning of the zinc layer causes a significant increase in absorption band intensity with time as the pure ZnSe substrate is exposed. The IR spectra of the exposed conversion-coated zinc (Figure 3.9b) shows similar spectral features, but in contrast to the pure zinc surface, water-induced reactions result in a band between 1150 and 850 cm$^{-1}$. Despite possible contributions from phosphate, the band maximum at ~1030 cm$^{-1}$ is in agreement with the bending vibrations of the ε-Zn(OH)$_2$ reaction product at ~1080 and 1025 cm$^{-1}$ and is assigned to the formation of less ordered zinc hydroxides$^{162}$. While the water band at ~1650 cm$^{-1}$ approaches a constant absorption level, the –OH band at ~3400 cm$^{-1}$ continues to increase with time due to an ongoing formation of zinc hydroxides$^{162,163}$. The smaller bands observed between 1550 and 1350 cm$^{-1}$ can probably be assigned to carbonate-containing reformation and oxidation products of the conversion layer.

The combined in situ ATR-FTIR Kretschmann and EIS measurements were performed on the conversion-coated zinc surface further coated with a film of a UV-curing polyester-acrylate upon exposure to 1 M NaSCN. Figure 3.10 shows some of the resulting IR spectra and Bode impedance plots along with the IR absorption intensity versus the exposure time for the band maxima at ~3400 and 1030 cm$^{-1}$, respectively.
According to the frequency-dependent characteristics of the Bode impedance plot obtained after short exposure times, the electrolyte penetrates quickly through the polymer film. In agreement with this, the IR spectrum displays a broad band at ~3400 cm\(^{-1}\) assigned to hydroxyl vibrations of water and of metal hydroxides within the conversion layer. The band observed at ~1650 cm\(^{-1}\) is assigned to molecular water, while the broad band below 1000 cm\(^{-1}\) is assigned to librations of water. The shape of the band at ~1650 cm\(^{-1}\) is obstructed by bands assigned to interfacial alterations and the band maximum is therefore difficult to follow as a function of exposure time. The bands observed at ~1530 and 1400 cm\(^{-1}\) are assigned to hydroxyl-carbonates formed within the surface film, but alterations of the polymer coating and organic components of the conversion coating may also contribute in this spectral region. During the first 3 hours of exposure, water is rapidly transported to the interface through the polymer layer, which also results in a fast increase in absorbance of the –OH stretching band at ~3400 cm\(^{-1}\). The peak observed at ~2100 cm\(^{-1}\) implies that also thiocyanate species are
present at the interface, i.e. that all electrolyte constituents pass through the polymer film to the hidden interface. The increase in the modulus of impedance observed at low and intermediate frequencies within the first 22 hours of exposure implies that alterations in the interfacial region impede the transport of electrolyte to the metal surface. In accordance with this observation, and with the result obtained for the pure conversion-coated zinc surface in Figure 3.9b, the water-induced alterations of the buried conversion layer are observed as a narrow IR band at ~1030 cm\(^{-1}\). This band shows a continuous growth during the course of the exposure. Between 22 and 34 hours of exposure, the decrease of modulus of impedance at intermediate to high frequencies indicates degradation of the system, probably connected with a partial delamination of the polymer film. As a probable result of the presence of reaction products that cover free metal surface and seal electrolyte pathways, the modulus of impedance at low and intermediate frequencies is subjected to an increase after around 34 hours of exposure. During the remainder of the exposure, the level of impedance varies with time, which implies an ongoing process of dissolution and reformation of the conversion layer and the corrosion products formed. The fact that the \(-\text{OH}\) vibration band at ~3400 cm\(^{-1}\) does not reach a maximum level can be explained both by an ongoing uptake of water and by a continuous contribution from metal hydroxides developed at the surface.

During the initial part of the exposure, the modulus of impedance may be used to roughly estimate the diffusion coefficient of the polymer coating according to Eq.10. Based on the modulus of impedance at the applied frequency of \(5\times10^4\) Hz at different exposure times and for the actual film thickness of ~11 \(\mu\)m, the diffusion coefficient was estimated to \(~1.7\times10^{-11}\) cm\(^2\)/s, which corresponds to a moderately protecting film. However, it should be remembered that surface processes at the metal surface contribute to the total capacitive response of the system and were early detected by ATR-FTIR Kretschmann. In order to obtain diffusion data for the attached polymer film from ATR-FTIR data, i.e. for Eq. 5 to be valid, the polymer was coated directly onto the ZnSe IRE and subsequently exposed to the electrolyte solution. This made it possible to extract an estimated diffusion coefficient of water according to Eq. 7. Figure 3.11 shows the ATR-FTIR spectrum of the UV-curing epoxy acrylate coated directly onto the ZnSe IRE and exposed for 125 hours to the electrolyte, along with the absorption intensity of the band at 3400 cm\(^{-1}\) as a function of time.

![Figure 3.11](image)

*Figure 3.11. (a) ATR-FTIR spectrum of the UV-curing polymer coated onto a ZnSe crystal after 125 hours exposure to 1 M NaSCN and (b) the IR absorption intensity at 3400 cm\(^{-1}\) as a function of time.*
In the absence of the metal film, the IR band at 3400 cm\(^{-1}\) mainly reflects the presence of water at the interface and was used for estimating the water diffusion coefficient. The negative bands are all in agreement with the spectrum of the dry polymer which implies a decreased polymer concentration within the depth of analysis as a result of polymer swelling and/or delamination\(^{164}\). For an actual film thickness of \(\sim 25 \, \mu m\), with an approximate value of \(A_\infty = 0.035\) absorption units, the diffusion coefficient was estimated to \(1.6 \times 10^{-11} \, \text{cm}^2/\text{s}\). This value is in agreement with the value extracted from EIS data, however it should be remembered that both methods neglect the influence of a non-random distribution of water, volume changes and the accumulation of water at the substrate / polymer interface.

To summarise, ATR-FTIR Kretschmann spectroscopy and EIS in combination was used to extract information about the hidden interface between surface-treated zinc and a polymer upon exposure to electrolyte media. Various system properties were distinguished, including the ingress of electrolyte constituents and an active process of water-induced alterations of the conversion layer with the formation of zinc hydroxide.

### 3.3.2.2. Silane-deposition on aluminium

The next step was to analyse the interface between a thermo-curing epoxy and an aluminium surface pre-treated with a silane film. Figure 3.12 first shows the ATR-FTIR spectrum of the silane system based on BTSE and \(\gamma\)-APS and pH-adjusted with acetic acid, deposited and baked directly onto the ZnSe IRE.

![Figure 3.12. ATR-FTIR spectrum of the mixed silane system deposited onto the ZnSe IRE and baked at 90 °C.](image)

The IR spectrum displays a band at 3700-3000 cm\(^{-1}\) assigned to \(-\text{OH}\) stretching vibrations of residual Si-OH groups not included in a Si-O-Si network, with contributions from residual water and symmetric and asymmetric N-H vibrations of the \(\gamma\)-APS. The bands between 3000 and 2800 cm\(^{-1}\) are assigned to the symmetric and asymmetric C-H vibrations of the silane, and to possible contaminants. The presence of acetic acid permits the ion pair formation between \(\text{CH}_3\text{COO}^-\) and \(\text{NH}_3^+\), which prevents the zwitterion-formation between \(\text{NH}_3^+\) and \(\text{SiO}^-\) and leaves the Si-OH functionalities free to form linkages to the metal surface and to condense.
into a denser Si-O-Si network. The acetate however contributes significantly to the IR spectrum, and the main part of the strong bands obtained at ~1575 and ~1410 cm\(^{-1}\) is not assigned to N-H but to COO\(^{-}\) asymmetric and symmetric stretching of amino acetate. The broad band between 1200 and 950 cm\(^{-1}\) is assigned to Si-O related bands, such as siloxane (Si-O-Si) linkages with chains of various lengths and branching, and to residual non-condensed Si-O-H. The high-wavenumber part of this band increases in intensity with the degree of cross-linking. This means that the band maximum at ~1160 cm\(^{-1}\) is assigned to BTSE siloxane linkages, while the band maximum at ~1050 cm\(^{-1}\) may correspond to the less highly cross-linked siloxane network of γ-APS (see Paper V). Residual unreacted Si-OH groups contribute at ~920 cm\(^{-1}\).

This study uses both ATR-FTIR Kretschmann and IRRAS spectroscopy, as is shown in Figure 3.13. The highly surface-sensitive IRRAS technique contributes with detailed information of the composition of thin surface films and also allows an estimation of the surface film thickness from comparison with calculated spectra. ATR-FTIR spectroscopy however enables interfacial analysis in the presence of a thicker polymer coating and also upon exposure to a bulk solution.

![Figure 3.13. The procedure used for ATR-FTIR Kretschmann and IRRAS spectroscopy on the same sample.](image)
Figure 3.14 shows the IRRAS and ATR-FTIR Kretschmann spectra on the same sample of aluminium-coated ZnSe deposited with the silane.

![IRRAS Spectrum](image1)

![ATR-FTIR Kretschmann Spectrum](image2)

**Figure 3.14. (a) IRRAS and (b) ATR-FTIR Kretschmann spectra of aluminium-coated ZnSe onto which the silane was deposited.**

The main spectral features of the two spectra are in agreement, but in the presence of aluminium also residual Al-OH resulting from the alkaline cleaning step may contribute to the spectrum at 3700-3000 cm\(^{-1}\) and below 1100 cm\(^{-1}\). The vibrations related to aluminium oxidation and hydration products appear to contribute more strongly to the ATR-FTIR Kretschmann spectrum than to the corresponding IRRAS spectrum. This is probably related to the fact that the ATR-FTIR Kretschmann analysis takes place through the metal film. While the maxima at 1110 and 1010 cm\(^{-1}\) are assigned to various Si-O bands, the band at 970-800 cm\(^{-1}\) is assigned to Al-O stretching or Al-O-H bending vibrations \(^{42, 148}\). Additionally, the bands in the low-wavenumber region show a suppressed intensity compared to the bands at higher wavenumbers. This suppression is due to the wavelength-dependent optical index of the aluminium film, which more strongly affects the electrical field strength at the metal / silane interface in the low-wavenumber region. Compared to the ATR-FTIR Kretschmann spectrum, the IRRAS spectrum shows a relative enhancement of the high-wavenumber side of the broad band at 1250-900 cm\(^{-1}\) and a decreased intensity of the smaller bands at lower wavenumbers. This is a common phenomenon observed in IRRAS \(^{169, 170}\) and is probably due to contributions to the dielectric function of the silane layer from both longitudinal and
transverse optical phonons to the ATR-FTIR spectra, while only longitudinal optical phonons contribute to the corresponding IRRAS spectra. For the same reason, the ATR-FTIR Kretschmann absorption bands appear to be shifted towards lower wavenumbers compared to the IRRAS spectrum.

Furthermore, a calculated IRRAS spectrum derived from the Fresnel equations and optical constants of each material were used to estimate the mean film thickness of the silane in the experimental IRRAS spectrum. This estimation was based on the absorption intensity of the Si-O-Si band maximum at ~1160 cm\(^{-1}\) and resulted in an estimated silane film thickness of approximately 800 nm. A silane film-thickness of about 700-900 nm was further confirmed by EDX imaging of a cross-section of a coated aluminium sheet (Figure 3.15).

![Figure 3.15. EDX mapping of a cross-section based on silicon (Si Kα1), displaying a silane film thickness of ~700-900 nm.](image)

In contrast to IRRAS, ATR-FTIR Kretschmann spectroscopy permits analysis at the hidden interface between the metal and a polymer. To provide a reference, the epoxy was applied directly onto a ZnSe IRE and was analysed by ATR-FTIR both prior to and after the thermal curing of the epoxy, as shown in Figure 3.16.

![Figure 3.16. ATR-FTIR spectrum of a pure ZnSe IRE coated with epoxy, both prior to curing (red) and after curing at 180 °C (black).](image)
The spectrum is complex, with bands related to aliphatic carbon chains (e.g. 3000-2800 cm\(^{-1}\)), the aromatic structure (1510 and 830 cm\(^{-1}\)) and various functional groups of the epoxy. The band maximum at \(~1700\) cm\(^{-1}\) is assigned to carbonyl groups (C=O) within the urea cross-linker. During thermal curing, neighbouring atoms to the carbonylic group react and form new types of amide linkages with a resulting shift towards 1720 cm\(^{-1}\). The remaining bands assigned to the epoxy show a higher intensity after curing. This means that there is a greater amount of the epoxy present within the depth of analysis, and confirms that the epoxy network is densified upon curing. Similar results were also obtained for a ZnSe IRE coated with both silane and epoxy. Figure 3.17 shows the ATR-FTIR spectra of cured epoxy on ZnSe in the absence and presence of an intermediate silane film, respectively.

![Figure 3.17. ATR-FTIR spectrum of only epoxy (red) and of both silane and epoxy (black) coated directly onto the ZnSe IRE after curing at 180 °C.](image)

In the presence of silane, a smaller amount of epoxy is present within the depth of analysis and the corresponding absorption intensity is lower. While it is still evident that a significant part of the epoxy film is analysed, the various Si-O-Si vibrations strongly contribute to the spectral region of 1200-950 cm\(^{-1}\). This means that the evanescent field holds a significant strength beyond the depth that constitutes the silane film-thickness.

Finally, Figure 3.18 shows the ATR-FTIR Kretschmann spectra of alkali-cleaned aluminium deposited with only epoxy, and with both silane and epoxy. Both systems are analysed both prior to and after the thermal curing.
Prior to curing, the broad strong band below 1100 cm$^{-1}$ is assigned to Al-O-related vibrations after the alkaline cleaning, with the aromatic backbone of the epoxy contributing to the sharp maximum at $\sim$830 cm$^{-1}$. In the absence of silane, most bands assigned to the epoxy experience an increased intensity, which means that an increased amount of the epoxy is present within the depth of analysis (i.e. a densification of the epoxy network upon curing). The band with a maximum at $\sim$1700 cm$^{-1}$ is assigned to carbonyl groups (C=O) within the urea cross-linker. In the presence of silane, the epoxy-related bands show smaller signals, with only the aromatic bands at $\sim$1505 and $\sim$820 cm$^{-1}$ being clearly detectable. This means that the actual depth of analysis in the presence of aluminium is of the same order of magnitude as the thickness of the underlying silane film. In the presence of silane, additional bands are observed at $\sim$1570 cm$^{-1}$ and $\sim$1410 cm$^{-1}$ assigned to the COO$^-$ groups of the acetate molecules associated with the silane. After curing, the decrease in intensity at 3700-3000 cm$^{-1}$ and 1100-950 cm$^{-1}$ and the increase at 950-700 cm$^{-1}$ can be assigned to the reformation of Al-O from Al-OH. In the absence of silane, the decrease in absorbance of the band at 1700 cm$^{-1}$ with a corresponding increase at $\sim$1720 cm$^{-1}$ is assigned to structural changes in the epoxy network. The increase in intensity of the epoxy-related bands is assigned to densification of epoxy within the depth of
analysis. In the presence of silane, any alteration assigned to the epoxy is difficult to deduce due to the small contribution of the epoxy film to the spectrum. However, in both spectra an additional band is observed at ~2220 cm$^{-1}$, assigned to stretching vibrations of cumulative C=N double bonds$^{168}$ formed as reaction-products of the urea–based cross linker of the epoxy at high temperatures$^{172}$.

Furthermore, the interaction between an electrolyte solution and the interface hidden between the metal and polymer coating was analysed with integrated in situ ATR-FTIR Kretschmann and EIS. Figure 3.19 shows the ATR-FTIR Kretschmann spectra obtained for the aluminium-coated ZnSe further coated with both silane and an epoxy top-coat upon exposure to 0.1 M NaCl, along with the IR absorption intensity of the band maximum at 3430 cm$^{-1}$ versus the exposure time.
Based on the data in Figure 3.18 it was established that the ATR-FTIR Kretschmann analyses performed in this study provide information of approximately 1 µm from the interface. Within one hour of exposure, hydroxyl (-OH) vibrations assigned to water and possible aluminium hydroxide formed were detected as a broad band between 3700 and 3000 cm\(^{-1}\) with a maximum at ~3430 cm\(^{-1}\). However, the presence of the water bending vibration band at ~1650 cm\(^{-1}\) was not observed until after ~7 hours of exposure, and the absence of a significant water-band below 1000 cm\(^{-1}\) throughout the whole exposure indicates a relatively small amount of bulk water at the interface.

Within 8 hours of exposure, both negative and positive changes in band intensities occurred in the spectral region below 1800 cm\(^{-1}\). The observation of sharp bands in agreement with the epoxy backbone implies that molecular reorientations and/or formation of epoxy reaction products are taking place. Negative bands could be assigned to swelling or delamination processes of the epoxy and silane, but also to material mixing in the silane / epoxy interfacial region. The negative band obtained at ~2230 cm\(^{-1}\) is assigned to the C=N-containing reaction products formed from the epoxy as a result of the high-temperature curing step and is not visible prior to curing of the epoxy (see Paper V). These reaction products may react with water and also vanish from the interfacial region. After 10 hours of exposure, the broad band below 1000 cm\(^{-1}\) with a maximum at 950 cm\(^{-1}\) indicates water induced alterations of the aluminium surface. The broad negative band observed at ~1050 – 1000 cm\(^{-1}\) is in agreement with the low-wavenumber spectral region of the siloxane network, assigned to more loosely bonded Si-O-Si (see Paper V), but changes in this spectral region can also be assigned to the structural alterations of the epoxy network. The corresponding Bode impedance plots obtained simultaneously are presented in Figure 3.20, along with the capacitance values at 1·10\(^{4}\) Hz versus the exposure time.
Figure 3.20. (a) EIS data for the aluminium film coated with silane and epoxy after 1, 8, 24, 45, 70, 89 hours exposure to 0.1 M NaCl displayed as Bode impedance plots, and (b) the capacitance at \(1 \times 10^4\) Hz versus the exposure time.

While the corresponding IR spectra (Figure 3.19) showed alterations within a few hours of exposure, the first alterations observed in the EIS data occurred after around 20 hours of exposure when the modulus of impedance showed a decrease in the high-frequency region as a result of water uptake in the polymer film. The corresponding increase in capacitance at \(1 \times 10^4\) Hz more clearly shows the lag-time that was observed for the EIS response. After 45 hours of exposure, a resistive behaviour at low frequencies could be verified from the Bode impedance plot, followed by small alterations assigned to ongoing surface processes.

In order to achieve a larger spectral response from the silane film, complementary analyses were performed with the silane solution deposited directly onto the ZnSe IRE followed by coating with epoxy. Despite the fact that ZnSe does not form strong bonds to the silane, which brings about poor adhesion properties, the increased depth of analysis and signal strength gained in the absence of the strongly absorbing metal film may add some valuable information on the system. In order to separate the spectral response of the epoxy and silane films, Figure 3.21 displays the ATR-FTIR spectrum of ZnSe coated with both silane and epoxy upon exposure to the electrolyte, along with the corresponding spectrum of ZnSe only coated with epoxy.
Figure 3.21. (a) ATR-FTIR spectra for the coated ZnSe substrates after 42 hours exposure to 0.1 M NaCl for coatings with silane and epoxy (red) and epoxy only (black) and (b) the respective absorption intensity of the maxima at 3380 cm\(^{-1}\) as a function of exposure time.

The initial fast increase in absorbance of the water-related band in the absence of silane probably results from some defect in the epoxy coating and the quality of the thin epoxy-films is of utmost importance for obtaining reproducible result. However, the presence of the silane film does seem to protect towards a point-wise penetration of water to the metal surface. Water in direct contact with ZnSe shows a different spectral appearance compared to water in contact with metal-coated ZnSe (Figure 3.1). While the maximum of the ~OH stretching vibration band at ~3380 cm\(^{-1}\) and the shoulder at 3230 cm\(^{-1}\) implies the presence of bulk-like water in both films, the spectrum of the pure epoxy shows an additional shoulder at ~3620 cm\(^{-1}\) assigned to non-hydrogen bonded liquid water within the polymer network. In addition to this, the relatively stronger band at 1650 cm\(^{-1}\) compared to the band at ~3380 implies that the character of the water in the epoxy film differs from the water within the silane film. The negative absorption bands observed at ~1510, 1180 and 830 cm\(^{-1}\) are in agreement with the spectrum of the dry epoxy backbone (Figure 3.16) and can be assigned to a replacement of epoxy by water within the depth of analysis. In the
presence of silane, the broad and strong negative band between 1050 and 950 cm\(^{-1}\) that cuts into the water band observed below 1000 cm\(^{-1}\) can be assigned to water-induced alterations within the silane film. While the original siloxane band of the dry film can be observed between ~1250 and 950 cm\(^{-1}\) (Figure 3.12), this alteration can probably be assigned to less densely bound Si-O-Si linkages that are more prone to swelling and/or hydrolysis, such as those belonging to a γ-APS siloxane network. The band simultaneously observed at ~910 cm\(^{-1}\) could be due to a formation of silanols (Si-OH) as a result from hydrolysis of Si-O-Si \(^{174}\). These results show that alterations of the siloxane network may contribute to the negative band obtained at ~ 1000 cm\(^{-1}\) in Figure 3.19 as discussed above.

To summarise, an amino-functional silane film on aluminium was characterised by both ATR-FTIR Kretschmann and IRRAS spectroscopy, and the ATR-FTIR Kretschmann set-up was further employed for studying interfacial interactions between this sample and an epoxy top-coat. Interfacial alterations were detected upon thermal curing of the epoxy, including the densification of the epoxy film, the dehydration of aluminium, and the formation of reaction-products assigned to the epoxy. The actual information depth analysed was found to reach from the metal surface to the inner parts of the epoxy layer. Finally, an integrated in situ ATR-FTIR Kretschmann and EIS analysis was performed to study the interactions between the polymer-coated sample and an electrolyte solution. The sensitivity of the ATR-FTIR Kretschmann technique was found to provide distinct absorption signals for very small alterations of the surface films. This however also brings about a high sensitivity for variations between samples. The spectral alterations connected to changes of the silane film were however small and the analysis was also subjected to spectral overlap of the absorption bands assigned to siloxane linkages and aluminium oxidation products, respectively. Complementary studies performed by in situ ATR-FTIR on pure ZnSe coated with silane and epoxy could however confirm a water uptake and water-induced alterations within the silane film.
4. Concluding remarks

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) in the Kretschmann geometry was explored for in situ studies of hidden metal / polymer interfaces. The ATR-FTIR Kretschmann technique was capable to monitor and to separate processes at the metal / polymer interface, including water sorption and transport of ionic species through the polymer film, as well as delamination and swelling of the surface-near polymer network. For aluminium, the oxidation and hydration processes were distinguished, and experiments on zinc allowed the determination of various hydroxyl carbonates. Other main processes identified were the swelling and/or delamination of the polymer network.

The technique was extended by integrating EIS as a complementary analytical tool. While ATR-FTIR Kretschmann analyses in the surface-near region, the electrochemical technique detects alterations of the whole system. The simultaneous use of ATR-FTIR Kretschmann and EIS was found both to give consistent results and to provide complementary information from the hidden metal / polymer interfaces upon exposure to an electrolyte, both with respect to information depth and deterioration processes identified. While swelling of the polymer network and delamination from the aluminium surface may be difficult to distinguish by ATR-FTIR Kretschmann, EIS can separate the two processes. On the other hand, while corrosion of aluminium and delamination may be difficult to distinguish by EIS, the formation of corrosion products can be detected by ATR-FTIR Kretschmann.

The combined ATR-FTIR Kretschmann and EIS set-up was further employed for interfacial characterisation and in situ studies of metal / polymer systems with a chromium-free pre-treatment applied to the metal. Various system properties were distinguished from the hidden interfacial region between conversion-coated zinc and a polymer upon exposure to electrolyte media. The phenomena observed included the ingress of electrolyte constituents and an active process of water-induced alterations of the conversion layer with the resulting formation of zinc hydroxide. Additionally, an amino-functional silane film deposited on alkali-cleaned aluminium was characterised, and the interfacial interactions between this sample and an epoxy top-coat were analysed upon thermal curing of the epoxy. The alterations observed included a densification of the epoxy film, the dehydration of aluminium, and the formation of reaction-products assigned to the epoxy. The actual depth of analysis was found to reach from the metal surface to the inner parts of the epoxy layer. The analysis with integrated in situ ATR-FTIR Kretschmann and EIS analysis upon exposure to electrolyte showed a high sensitivity of the ATR-FTIR Kretschmann technique to very small alterations in the interfacial region. Complementary in situ ATR-FTIR studies on ZnSe in the absence of a metal film confirmed a water uptake and water-induced alterations within the silane film.

To conclude, the examples presented provide evidence of the potential of ATR-FTIR Kretschmann spectroscopy, which offers information to be gained from a hidden interface between a metal and a polymer coating. The technique can be a valuable tool for obtaining a deeper understanding of early deterioration mechanisms of technically important metal / polymer systems, also in the presence of a surface pre-treatment.
5. Future work

In this work, ATR-FTIR Kretschmann spectroscopy was applied for studies of metal / polymer interfaces upon exposure to water and electrolytes, alone and in combination with EIS. The methodology was further used to study the systems upon exposure to corrosive conditions in the presence of a surface pre-treatment; e.g. a Ti-based conversion system for zinc and a thick silane film applied on aluminium.

The ATR-FTIR Kretschmann technique alone, or integrated with electrochemical method, could considerably contribute to increase the knowledge of various surface processes at hidden metal / polymer and metal / liquid interfaces within several areas of interest, e.g. in the transport, building and medical industries.

In order to extend the applicability, the methodology would however benefit from further studies regarding the optimal experimental conditions with respect to the metal film thickness and polarisation of light. Also the properties of the thin metal film should be more carefully analysed with respect to optical properties, porosity, and degree of oxidation compared to the respective bulk material, as well as of the effects of surface roughness.

ATR-FTIR Kretschmann spectroscopy could also be combined with electrochemical mapping techniques, including scanning vibration electrode technique, local electrochemical impedance spectroscopy and scanning Kelvin probe, where the scanning Kelvin probe also allows studies upon exposure to humid air.
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Maria Öhman
Stockholm, November 2010
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Errata

Development of ATR-FTIR Kretschmann Spectroscopy for In situ Studies of Metal / Polymer Interfaces

and its Integration with EIS for Exposure to Corrosive Conditions

by Maria Öhman

- p.iii line 23, p.1 line 27, p.15 line 19  
  electrical ⇔ electrochemical

- p.20, line 30

  bis[3-triethoxysilylpropyl]ethane ⇔ bis-1,2-(triethoxysilyl)ethane

- p.20, Figure 2.2

  Replace figure with:

  [Chemical structures]

- p.56, Ref 40

  Author = G.E. Thompson

- p.58, Ref 112

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