

Water and Ions at Polymer/Metal Interfaces

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Abstract The adsorption and transport of water and ions at polymer/metal interfaces has a strong impact on the adhesion of the polymer as well as on the kinetics of corrosive degradation. Although not directly correlated both wet-de-adhesion and corrosive de-adhesion are accelerated by water enrichment at the interface which promotes the ingress of ions. The discussion of these phenomena starts with the consideration of the adsorption of water on oxide surfaces, as all engineering metals are covered with an ultra-thin atmospheric oxide film, and ends with the cathodic and anodic corrosive de-adhesion mechanisms of polymers from oxide covered metals. The bridge between the water adsorption and corrosive de-adhesion reactions is built based on the separation of water and ion transport in polymeric interphases and the discussion of diffusion and migration as the principal processes.

Keywords Adsorption • De-adhesion • Water • Ions • Interface • Delamination • Spectroscopy • Interface electrochemistry • Migration • Diffusion • Corrosion

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1 Introduction

Corrosive de-adhesion processes at polymer coated metal compounds are commonly connected with the interfacial incorporation of water and hydrated ions. H_2O can indeed diffuse directly through the organic matrix, but most coatings nevertheless provide an effective barrier for ion transport based on low dielectric constants and small free volumes of the macromolecular network. In contrast, defects in organic films which penetrate to the metal result in a three phase boundary between aqueous phase, polymer and substrate surface and consequently allow an incorporation of H_2O and hydrated ions along the polymer/oxide/metal interface. Corrosion is initiated at interface sections adjacent to the electrolyte covered defect in the presence of atmospheric oxygen. The present chapter consequently focuses on the aspects of water incorporation at polymer/metal interfaces, on the transport of hydrated ions along the interface, and on thereby induced cathodic as well as anodic de-adhesion processes.

2 Water at Polymer/Oxide Interfaces

2.1 Water Adsorption on Oxide Surfaces

The interaction of water with metal and metal oxide surfaces plays an important role in many interface-governed processes such as adsorption/desorption, heterogeneous catalysis, de-adhesion of polymers and corrosion. From catalytic nanoparticles to the surfaces of engineering alloys all metallic surfaces except that of noble materials are covered with mono- and multiphase, crystalline or amorphous oxide films. Once water molecules reach the polymer/oxide interface, they do not only deteriorate the oxide structure via the formation of metal hydroxides and oxyhydroxides, but also significantly change the properties of the bulk polymer and alter the attractive interactions at the interface.

In general, the surfaces of complex alloys are covered with the native oxides of the alloying elements, for example with those of iron, zinc, aluminium, titanium, copper and magnesium. Due to thermodynamic and kinetic effects such as formation energies, diffusion rates and oxidation affinity, the surface chemistry of alloys usually differs from that of the bulk material.

A profound understanding of the interaction mechanisms with water requires fundamental investigations on single crystalline oxide surfaces of the respective metals. Depending on parameters like temperature or $\text{H}_2\text{O}/\text{O}_2$ partial pressure during preparation, water will be present on oxide surfaces as molecular H_2O or it may dissociate and form surface hydroxyls. As an adsorbate, water can interact with clean and hydroxylated metal oxide via electrostatic forces or charge transfer reactions and may form hydrogen bonding networks [1].

On Al-terminated α -Al₂O₃ (0001) surfaces, for example, the dissociative adsorption of water has been experimentally and theoretically demonstrated [2–10], but the termination itself is still under discussion. Experiments performed in ultra-high vacuum indicated that α -Al₂O₃ (0001) is either covered with Al [11] or with a combination of Al and O [12]. Crystal truncation rod diffraction studies proved an oxygen terminated, hydrated α -Al₂O₃ (0001) surface with a 53 % contracted double aluminium layer directly below [10]. A molecularly adsorbed water layer was detected about 2.4 Å above the terminal oxygen. Moreover, it was reported that dissociative adsorption of H₂O with low surface mobility is predominant for low degrees of coverage, whereas complex structures of mixed dissociatively as well as molecularly adsorbed water layers should be expected for high coverage levels.

Various studies also focused on the interaction of H₂O with low index surfaces of MgO. Due to the observed reversibility of adsorption isotherms, water has long been considered to adsorb on MgO (001) in a non-dissociative manner [13]. It was also suggested that dissociative adsorption can be only facilitated in the presence of surface defect sites [14]. Recent theoretical work, however, indicated that defects are not required to induce water dissociation [15, 16]. Moreover, it was shown that a certain threshold of water activity is necessary to convert MgO from a state of low, defect-mediated hydroxylation to a fully OH-covered surface [17]. A combined experimental-theoretical investigation proved that initial hydroxylation results in the formation of isolated OH groups and that surface roughening occurs if the water pressure is increased. It points at a mechanism that includes the hydrolysis of Mg–O bonds [18]. This means that extensive hydroxylation should not result in an unstable state of the (001) surface for both MgO bulk and thin films [18].

For some oxides, however, even intense investigations were not sufficient yet to adequately verify possible adsorption mechanisms, for example for the interaction of water with the ideal rutile TiO₂ (110) surface [1, 19, 20]. Experimental results indicate that molecular chemisorption dominates at low temperatures in ultra high vacuum for all degrees of coverage [18, 21, 22], but according to computational studies, dissociative adsorption of water should be the most favorable mechanism for sub-monolayer coverage [23, 24].

2.2 Molecule and Polymer Adsorption on Water Covered Metal Oxides for the Investigation of Adhesion Forces

For aluminium, joining by means of welding is rather challenging and bolting/riveting is connected with the disadvantage of increased weight and non-homogeneous stress distribution. Hence, adhesive joining is a very important technological process for the design of light-weight and durable composite structures based on aluminium and aluminium alloys.

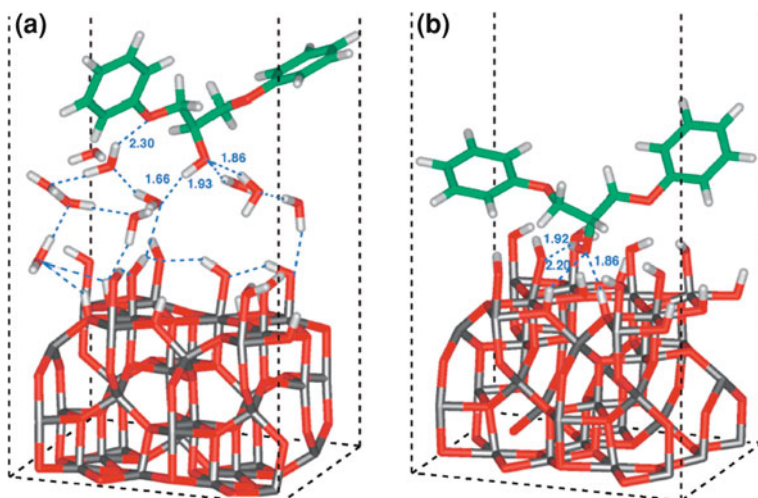


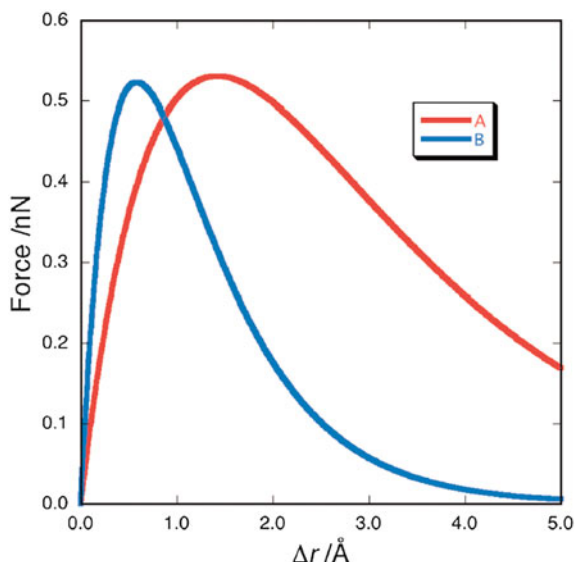
Fig. 1 Optimized structures of adhesive-adherent complexes of (a) hydroxylated γ -alumina (001) surface with adsorbed water molecules and (b) hydroxylated γ -alumina (001) surface without adsorbed water molecules (Reprinted with permission from Ref. [25]. Copyright 2012, The Chemical Society of Japan)

In this context, theoretical calculations are state-of-the-art to evaluate the resulting adhesion forces. As an example, Fig. 1 illustrates the results of a density functional theory based study that focused on the interaction of diglycidylester-bisphenol (DGEBA) molecules with hydroxylated γ - Al_2O_3 surfaces in the presence and in the absence of a molecular water layer at the interface [25, 26]. For both systems, hydrogen bond formation dominated the interaction mechanism. It results in adhesive energies of 117.5 kJ/mol with and of 66.0 kJ/mol without a molecular water layer. The increased adhesion interaction energies are assigned to a higher number of hydrogen bonds that formed in the presence of water molecules at the interface [25].

The calculated force-distance curves presented in Fig. 2 indicate similar maxima at 0.53 nN and 0.52 nN for water-containing and water-free systems. The shift of the maximum to larger distances refers to a “buffering effect” of molecular water against the shear force of adhesion due to an increased mobility of the H_2O layer. Stress required to peel the adhesive from the surface was evaluated by dividing the maximum force to the projected unit area of the DGEBA molecule. The analysis yielded a maximum adhesion stress of 5.1×10^2 MPa when water was present and of 5.0×10^2 MPa when water was absent. In summary, it was interpreted that H_2O indeed causes higher adhesive interaction energies, but does not induce increased adhesion strengths due to its high mobility at the interface [25].

Taking the next step in the simulation of polymer coatings on metal oxides, the adsorption of epoxy adhesive components on γ - Al_2O_3 surfaces was investigated with a density functional theory based tight binding method [27]. It was focused on diglycidylesterbisphenol (DGEBA), on diethyltriamine (DETA) as well as on the

Fig. 2 Calculated force-distance curves for models of adhesive-adherent complexes on the γ -alumina (001) surface (a) with and (b) without adsorbed water. (Reprinted with permission from Ref. [25] Copyright 2012, The Chemical Society of Japan)



adhesion promoter 3-aminopropylmethoxysilane (AMEO) and shown that the condensation reaction of AMEO via its silane group is favorable compared to those of DGEBA and DETA. Moreover, the process proceeds highly exothermic and with negligible barriers, whereas the reaction of DGEBA depends on the opening of one epoxy ring in the molecule prior to condensation. The curing agent DETA interacts via its amine group with surface hydroxyls and its condensation reaction is highly endothermic. These theoretical results correlate well with the experimental findings which indicate an enrichment of the AMEO molecules at the interface, even when only minor AMEO amounts were added to the polymer formulation [28]. A detailed theoretical analysis of the reaction mechanisms of DGEBA, DETA and AMEO molecules on γ - Al_2O_3 surfaces was based on two possible adsorption sites and focused on the effect of neighboring adsorbates on the adsorption thermodynamics. The structure of the hydroxylated γ - Al_2O_3 surface, the definition of the two adsorption sites and the investigated reaction paths are shown in Figs. 3 and 4 [29].

As seen in Table 1, the presence of neighboring adsorbates results in a significant decrease of most of the condensation barriers. This observation is explained by the creation of movable dipole moments and excess protons which can stabilize the transition states. It also indicates that the presence of proton donors such as physisorbed water molecules effectively support the activation of new reaction routes, for instance by a stabilization of the dangling bonds of opened epoxy rings of DGEBA [29]. Interestingly, silanol type adhesion promoters like AMEO are not affected by this mechanism. Thus, their effect on the interfacial adhesion force cannot be solely explained by the creation of a higher density of interfacial bonds, but in addition by a formation of bonds that are independent of the presence of neighboring adsorbates [29].

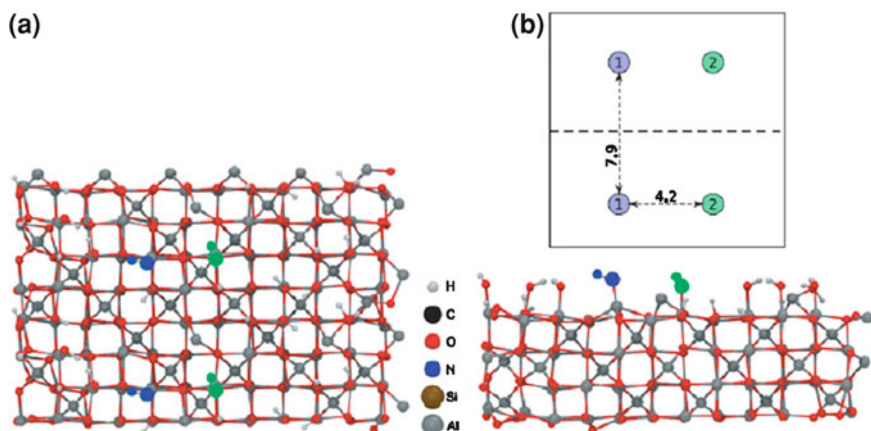


Fig. 3 **a** Views along the (00-1) (*left*) and (010) (*right*) directions of the hydroxylated γ - Al_2O_3 surface model. The adsorption site 1 is marked blue, site 2 is marked green (Reprinted with permission from Ref. [29], Copyright 2012, Springer). **b** Schematic of investigated adsorption sites in the γ - Al_2O_3 supercell and corresponding distances (in Å) (Reprinted with permission from Ref. [29], Copyright 2009, Springer)

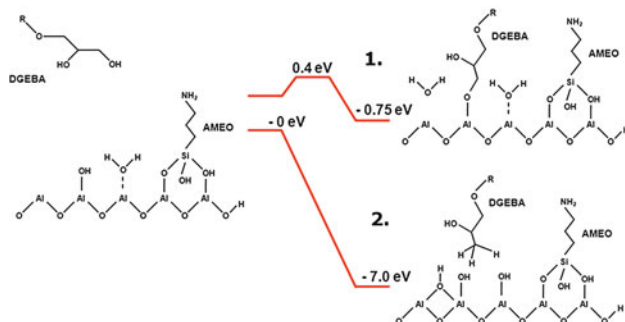
For the fundamental analysis of polymer adsorption on metal oxides, combined theoretical and experimental approaches were shown to be promising. As an example, the adhesion of acrylonitrile-butadiene (ABS) on copper and copper oxide surfaces was studied by force field calculations and scanning force microscopy to reveal the applicability of poly(styrene-co-acrylonitrile) (SAN) and poly(styrene-alt-maleic anhydride) (SMAh) as model copolymers for adhesion promotion (see Fig. 5a) [30, 31].

Equivalent adhesion forces on metallic copper of around $\sim 0.5 \text{ J/m}^2$ were detected for SMAh, oxidized SAN as well as for the model polymers ABS and polybutadiene (pBd). However, except for SAN, a strong increase in the work of adhesion was observed when the molecules specifically interacted with oxygen atoms on the substrate surface (see Fig. 5b). SMAh adsorption exhibited the highest work of adhesion and consequently turned out to be the most promising candidate for adhesion promotion [30].

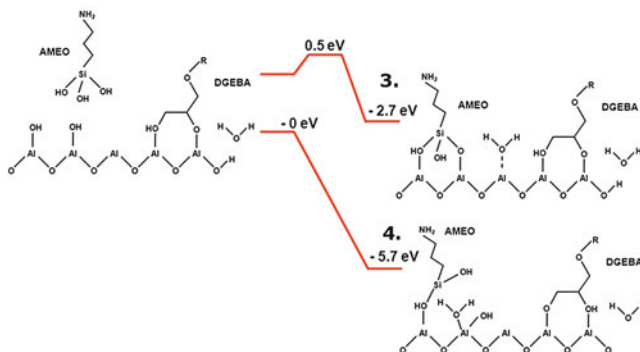
2.3 Molecular Understanding of Macromolecule/Oxide Interactions in Water Rich Environments

It is generally accepted that polymer chains are able to form covalent bonds with the oxide surface if the hydrocarbon backbone does not contain polar or charged functional groups. As long as no adhesion promoting molecules are present in the polymer matrix or included in a pre-treatment layer on the substrate, the adsorption

Case 1: DGEBA at site 1 with AMEO and condensed water at site 2



Case 2: AMEO at site 1 with DGEBA and condensed water at site 2



Case 3: DGEBA at site 1 with DGEBA and condensed water at site 2

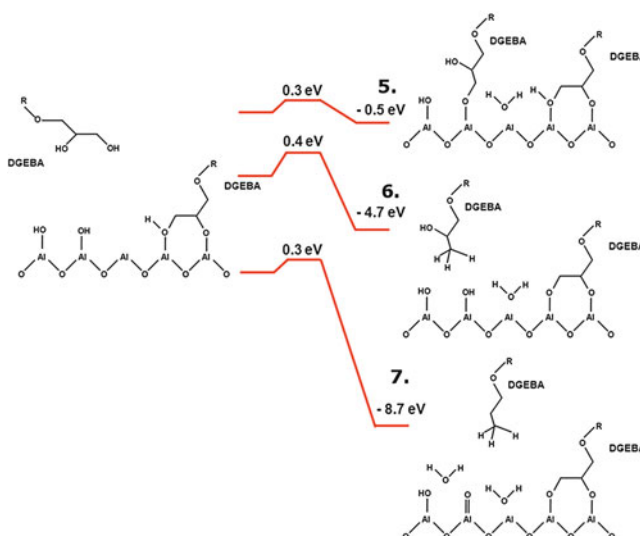


Fig. 4 Possible reactions of DGEBA and AMEO in the presence of pre-adsorbed molecules, illustrating that the presence of proton donors such as physisorbed water molecules can be advantageous in enabling new reaction routes (Reprinted with permission from Ref. [29], Copyright 2009, Springer)

Table 1 Reaction pathways and respective barriers for the co-adsorption of DGEBA and AMEO

Comp. 1	Comp. 2	Mechanism	Mech.	E_r^{sngl}	$E_{\text{barr}}^{\text{sngl}}$	E_r^{co}	$E_{\text{barr}}^{\text{co}}$
AMEO + H ₂ O	AMEO	Condensation	–	–4.1	~0	–3.2	~0
	DGEBA	Condensation	1	–0.4	2.1	–0.8	0.2
		OH abstraction	2	–	–	–7.0	~0
AMEO + OH DGEBA	DGEBA	Condensation	–	–0.4	2.1	–0.4	0.2
	AMEO	Condensation	3	–4.1	~0	–2.7	0.5
		OH abstraction	4	–	–	–5.3	~0
	DGEBA	Condensation	5	–0.4	2.1	–0.3	0.3
		Single OH abstraction	6	–	–	–4.7	0.4
		Double OH abstraction	7	–	–	–8.7	0.3

Comp. 1 are the components already present at site 2 from the first adsorption reaction, comp. 2 are the newly adsorbed components. E_r^{sngl} , $E_{\text{barr}}^{\text{sngl}}$ list the isolated adsorption reaction energies and barriers for comp. 2 E^{co} reflect the respective reaction energies and barriers for the co-adsorption scenario. All energies are reported in eV. (Reprinted with permission from Ref. [29], Copyright 2009, Springer)

of macromolecules on oxide surfaces occurs via non-specific van-der Waals interactions [32]. From the perspective of the adhesion of macromolecules, enrichment of water at the polymer/oxide/metal interface on the one hand is problematic, because water molecules can replace polymer-metal/metal-oxide bonds. This can result in wet and/or corrosive de-adhesion [33–36]. On the other hand, for the design of biocompatible materials long-time stability under physiological conditions is a very relevant performance requirement. The prevention of proteins and other macromolecules from adhesion is consequently of crucial importance. Therefore, a profound understanding of the elementary processes of adhesion and de-adhesion at polymer/oxide/metal interfaces is a prerequisite for the design of novel polymer/nanoparticle composites, biocompatible materials, protective polymer coatings as well as high-strength adhesive joints.

The investigation of de-adhesion processes at polymer/metal interfaces and the development of interface-sensitive experimental approaches has been an active area of research during many decades [37–42]. For polymer films on metal electrodes, electrochemical impedance spectroscopy (EIS) was demonstrated to be a versatile tool for the monitoring of water uptake kinetics and the diffusion coefficient of water [41, 43–49]. Alternatively, attenuated total reflection infrared spectroscopy (ATR-IR) [50] can be used to determine water penetration of polymer films with high interfacial sensitivity [50]. It allows for an identification of different interaction modes of water at the interface, such as the formation of clusters or molecular water layers, hydrogen bonding between the polymer and water as well as surface hydroxylation of the metal oxide [37, 40, 41, 51–53]. Additionally, it is sensitive to the local environment of the adsorbates and shows deviations in peak locations, shapes and intensities. This offers insights into lateral interactions, vibrational coupling effects, binding modes as well as into molecular conformation and orientation [54]. Additional information about (in situ) adsorption/desorption and adhesion/de-adhesion processes at buried interface may

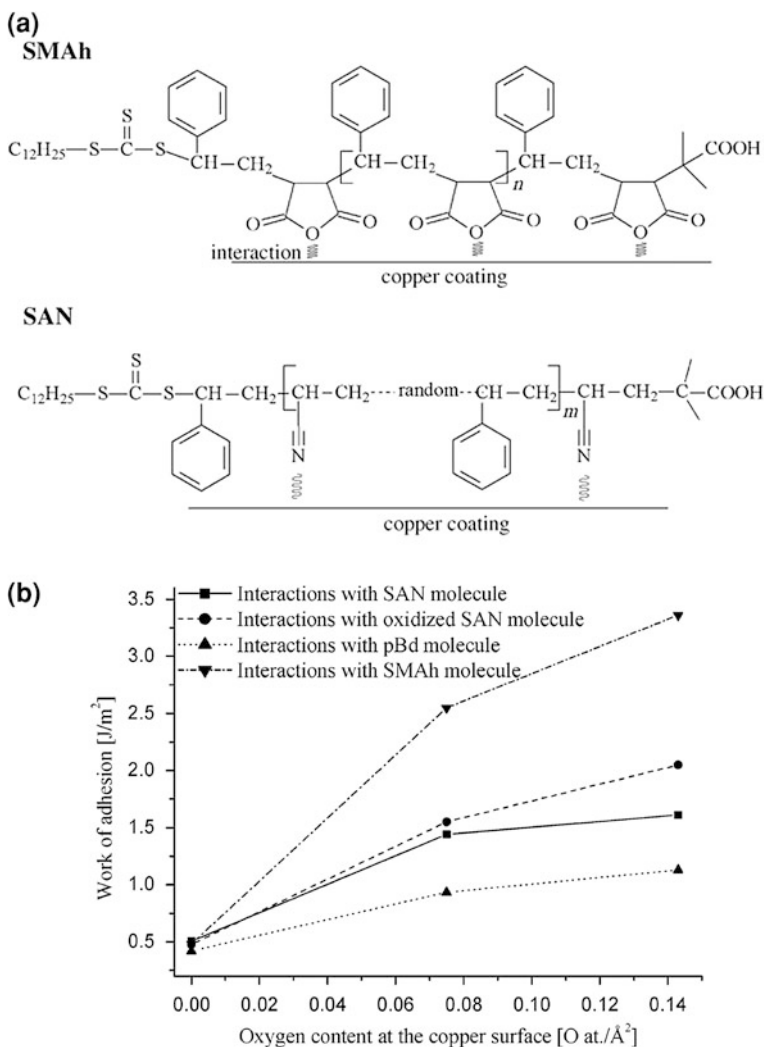


Fig. 5 **a** Schematic illustration of the chemical structure of the SMAh and SAN copolymers and their potential interaction with copper coatings (Reprinted with permission from Ref. [31], Copyright 2006, Wiley-VCH). **b** Values for the work of adhesion between single SAN, oxidized SAN, polybutadiene, and SMAh molecules with pure copper surface and oxygen-modified copper surfaces (Reprinted with permission from Ref. [30], Copyright 2007, American Chemical Society)

be obtained employing surface enhanced infrared absorption spectroscopy as well as surface enhanced Raman spectroscopy [42, 54]. Moreover, the water uptake of polymer films can be investigated by combined setups for simultaneous ATR-IR and EIS measurements [41].

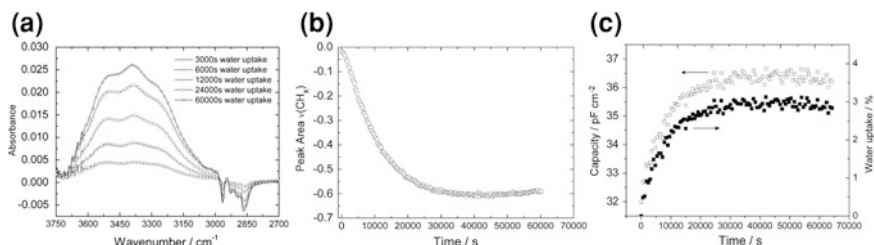


Fig. 6 **a** Increase of the H₂O-peak area in the interphasial adhesive layer during water uptake ($D = (2.0 \pm 0.2) \times 10^{-9} \text{ cm}^2/\text{s}$). **b** Decrease of the CH_x-stretching peak in the interphasial adhesive layer during water uptake. **c** Capacitance change (measured at 10 kHz) and calculated water uptake for a defect-free adhesive film (Reprinted from Ref. [41], Copyright 2007, with permission from Elsevier)

Figure 6 illustrates experimental data generated with such an approach. Shown are area changes of H₂O (a) and CH₂ (b) stretching vibration peaks of a defect-free epoxy film adsorbed on a silicon substrate during the exposure to borate buffer solution. Capacitance and water uptake profiles obtained by EIS were recorded simultaneously (see Fig. 6c). The CH₂ peak intensity decreased by 4–5 % at maximum, which indicates that wet de-adhesion of the macromolecular film did not take place during water uptake. Moreover, equivalent coefficients for H₂O diffusion through the polymer layer were determined by ATR-IR and EIS: $2.0 \times 10^{-9} \text{ cm}^2/\text{s}$.

For a more realistic simulation of technical interfaces, thin metal or oxide films can be deposited on surfaces of the internal reflection elements used for ATR-IR spectroscopy prior to coating with a polymer [40]. The diffusion of water through a two component model adhesive (nitrile rubber and vinylchloride-vinylacetate copolymer) film, for example, was recently investigated using aluminium deposited on ZnSe ATR crystals [40]. Peak area changes indicating an increased water activity at the polymer/aluminium interface (O–H stretching vibrations at $3,450 \text{ cm}^{-1}$, O–H bending vibrations at $1,650 \text{ cm}^{-1}$, and Al–O-/Al–OH-vibrations detected at 960 cm^{-1} , see Fig. 7b) reflected saturation curves (see Fig. 7a) [51]. While exposed to one molar NaSCN solution, the transport of thiocyanate ions through the macromolecular layer was tracked by monitoring of the C = N vibration signal at $2,075 \text{ cm}^{-1}$. In contrast to the development of the peak areas for water as shown in Fig. 7a, the C = N signal intensity increased linearly and thereby confirmed that different mechanisms determine the transport of thiocyanate and H₂O [51].

These results were complemented by a combined ATR-IR/EIS study of structural adjustments occurring at aluminium/polymer sample systems during the exposure to one molar NaSCN solution [53]. It shows that simultaneously recorded infrared and electrochemical impedance spectra provide important additional information. Figure 8a–d illustrates time-resolved intensity changes of the peaks detected at $3,450$, $1,650$, $2,075$ and 950 cm^{-1} for an aluminium surface coated

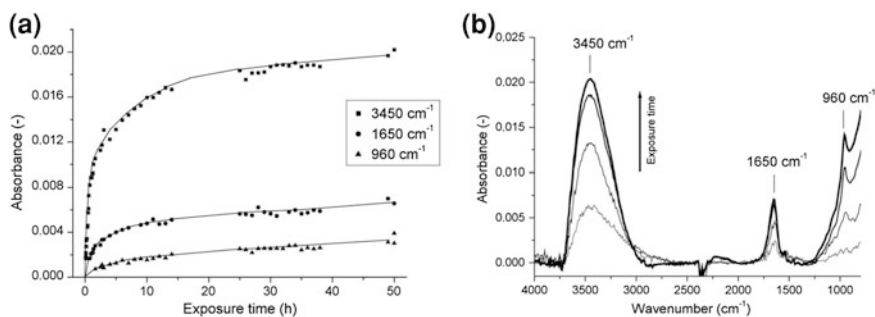


Fig. 7 **a** IR absorption intensities at 3,450, 1,650 and 960 cm^{-1} versus the exposure time for the ZnSe element coated with a thin aluminium film and a polymer film in contact with ultra pure deionized water. **b** ATR-FTIR spectra of a ZnSe element coated with a thin aluminium film in contact with ultra pure deionized water. The exposure times were 40, 163 min, 26 and 50 h, respectively. The ATR-IR absorption peak at 1,650 cm^{-1} stays constant during exposure to water (see Fig. 8b) and thus allows a substrate independent analysis of water uptake on the aluminium oxide film (Reprinted from Ref. [51], Copyright 2006, with permission from Elsevier)

with a transparent alkyd based polymer layer [53]. The corresponding impedance data are presented in Fig. 8e. It is observed that the ingress of H_2O into the polymer film caused a rapid change of the infrared absorbance intensities of the water and hydroxyl stretching bands centered at 3,450 cm^{-1} . The plateau in the impedance curves recorded at low frequency values indicates the presence of pores and small defects in the macromolecular coating. The Al–O and Al–OH vibration peak at 950 cm^{-1} appeared delayed, because a minimum threshold water activity level at the polymer/aluminium interface has to be achieved before oxidation and hydroxylation reactions can initiate. Changes in the absorption signals at 1,650, 3,450 and 950 cm^{-1} show a clear deviation from what has to be expected for Fickian diffusion driven processes, because after approximately 34 h of exposure, a quick and linear increase of the peak intensities is observed. The impedance data in turn reflect an abrupt decline of the film resistance after 34 h of exposure. This confirms distinctly changed water uptake kinetics and indicates the onset of delamination/wet de-adhesion of the polymer layer [53].

3 Ion Transport at Polymer/Metal Interfaces

Once water and hydrated ions are present at polymer/metal interfaces, additional electrochemical processes such as interfacial transport of charged species can initiate and result in corrosive degradation. For polymer coated iron or zinc substrates, for example, de-adhesion of organic films occurred to be often dependent on the cathodic delamination mechanism. It depends on the formation of galvanic cells at the interface with locally separated electrodes, local reduction of O_2 and

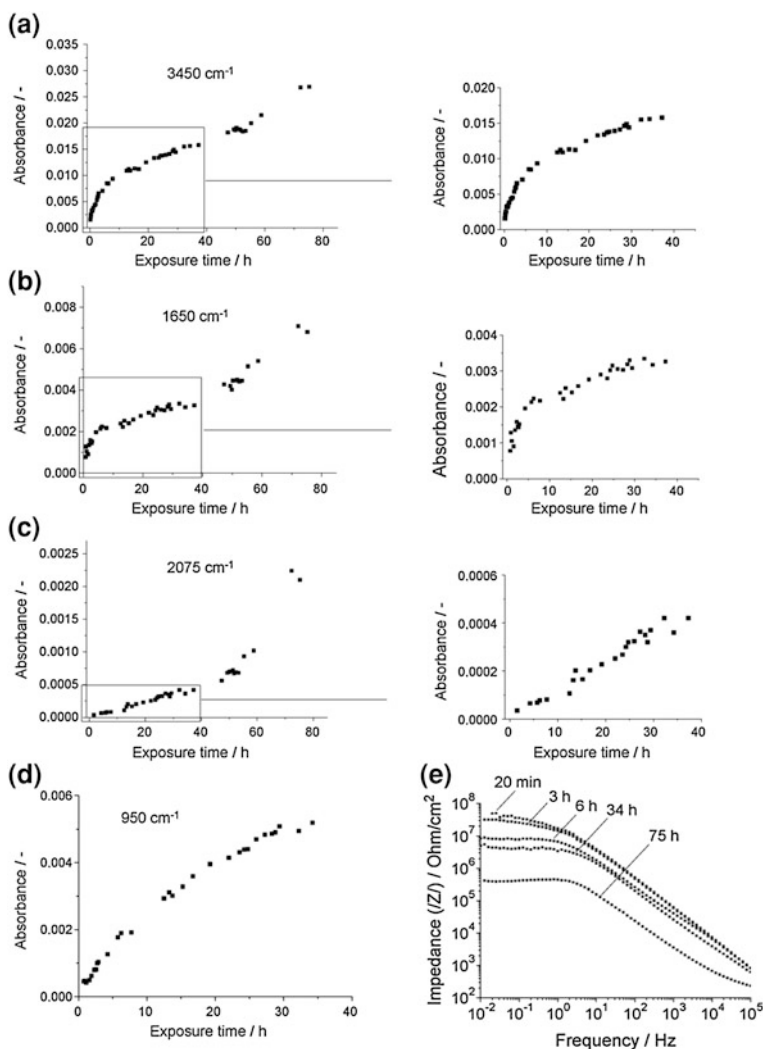


Fig. 8 The absorption intensity versus the exposure time for the ZnSe element coated with a thin aluminium film and a transparent alkyd varnish in contact with a 1 M NaSCN solution for the peaks (a) 3,450 cm⁻¹ (b) 1,650 cm⁻¹ (c) 2,075 cm⁻¹ (d) 960 cm⁻¹ and (e) the corresponding electrochemical impedance spectra at different exposure times. The ATR-IR absorption intensities at 1,650 and 3,450 and 950 cm⁻¹ shows a deviation from Fickian behavior, which is in good agreement with the sudden drop in impedance values indicating wet de-adhesion/delamination of the polymer film (Reprinted from Ref. [53], Copyright 2007, with permission from Elsevier)

requires ion transport for charge compensation. Theoretical concepts that sufficiently describe and predict these processes are hardly available due to the complexity of polymer/substrate interface structures. Basic aspects were adopted

from mechanistic considerations developed for bulk electrolyte solutions or idealized model geometries, but still require comparison with experimental observations made at technically relevant interface systems. Therefore, the following paragraphs briefly introduce some background concepts prior to the presentation of the fundamentals of corrosive delamination.

3.1 The Fundamentals of Hydrated Ion Transport: Ion Diffusion, Ion Migration in an Electric Field & Electro Kinetics

Corrosion processes are usually dependent on the formation of a galvanic cell with separated local anode and cathode in contact with a conductive electrolyte. Electrons are exchanged via a metallic connection and the circuit is completed by a transport of ions in bulk electrolyte to compensate the generated charge surplus near the electrodes. Such transport is enforced by an electric field E that exerts a force $|\vec{F}_E|$ on ions of species i with a charge $z \cdot e$ (e : elementary charge):

$$|\vec{F}_E| = z_i \cdot e \cdot |\vec{E}| \quad (1)$$

Anions are accelerated towards the anode and cations move towards the cathode. However, ion transport through an aqueous solution will be decelerated by a rising friction force $|\vec{F}_R|$ with increasing transport velocity:

$$|\vec{F}_R| = 6\pi \cdot r_i \cdot \eta \cdot |\vec{v}_i|$$

(r_i : radius of ion species i , η : solvent viscosity, $|\vec{v}_i|$: velocity of ion species i) [55]. A constant transport rate will be achieved for

$$|\vec{v}_i| = \frac{|\vec{F}_E|}{6\pi \cdot r_i \cdot \eta}$$

and directly affects the electrolytic conductivity of a salt solution. The mobility of ion species i in bulk water is strongly determined by parameters such as ion concentrations and interionic interactions [55]. For aqueous electrolytes especially the dipole properties of H_2O molecules play an important role. Dependent on the electrostatic field that results from ion charge and ion radius, H_2O species form solvation shells of different structure and spatial dimensions. Na^+ for example exhibits an ion radius of around 0.097 nm and thereby generates a stronger electric field than K^+ with a radius of around 0.133 nm. The number of water molecules that form the hydration shell of Na^+ is 7–8 and consequently larger than for K^+ , which is 4–5 [55]. This leads to increasing hydrodynamic radii for alkali cations in the order $Cs < Rb < K < Na < Li$ and is correlated with a decreasing ion mobility at polymer/oxide/metal interfaces.

Exceptional effective charge transfer between the electrodes of a galvanic cell can be achieved with acid and alkaline solutions due to a fast diffusion of protons between H_2O molecules. For high ion concentrations in delaminated areas of polymer coated metal compounds, ion-ion interactions additionally affect the mobility of charged species. Coulomb attractions promote the generation of short range orders between a central ion and hydrated ions of opposite charge encircling it. Brownian motion indeed counteracts such formation of ordered structures within the bulk electrolyte, but cannot fully compensate the process if cations and anions are accelerated in opposite directions due to the electric field of a galvanic cell. In that case, the short range order gets distorted and will be continuously re-arranged, which takes some time. The central ion therefore moves ahead its ‘cloud’ of counter ions and is retained. As contrary charged species are accelerated in opposite direction by the external electric field, the central ion moves additionally decelerated due to electrophoretic effects [55–58].

Ion transport processes are not only affected by electrostatic forces, because inhomogeneous ion distributions are released by diffusion, as well. The proportionality of particle flow J and concentration gradient $\delta c/\delta x$ is expressed by Fick’s first law. Moreover, the particle flow is dependent on the particle (drift) velocity $|\vec{v}|$ as well as on the concentration c :

$$J = |\vec{v}| \cdot c = -D \frac{\delta c}{\delta x} \quad (2)$$

(D : diffusion coefficient) [56]. The thermodynamic force $|\vec{F}|$ for particle movement arises from an inhomogeneous distribution of species i , which results in a locally different chemical potential μ_i [56]:

$$|\vec{F}| = - \left(\frac{\delta \mu_i}{\delta x} \right)_{p, T \text{ const}}$$

(x : respective location in the first dimension, T : temperature, p : atmospheric pressure). Taking the chemical potential $\mu_i = \mu_{i0} + RT \ln(a_i)$ for species i into account (μ_{i0} : chemical potential for standard conditions, R : universal gas constant, a_i : activity of species i), the following equation results:

$$|\vec{F}| = -RT \left(\frac{\delta \ln(a_i)}{\delta x} \right)_{p, T \text{ const}}$$

For ambient conditions, the atmospheric pressure and temperature can be expected to remain constant, and for ideal solutions a_i can be replaced by the concentration c_i of species i . With application of Eq. 2 the resulting drift velocity can be additionally attributed to the contributions of concentration gradients and external forces [56]:

$$|\vec{v}_i| = - \frac{D \delta c}{c_i \delta x} = \frac{D}{RT} \cdot |\vec{F}|$$

If species i moves in an external electrostatic field, its force $|\vec{F}|$ can be specified by the electric force $|\vec{F}_E|$ of Eq. 1. In that case, the drift velocity is equivalent to the ion velocity introduced for Eq. 2. The resulting effective ion mobility then is (F = Faraday constant) [56]:

$$\frac{|\vec{v}_i|}{|\vec{E}|} = \frac{z_i \cdot F \cdot D}{RT}$$

Even if no external electric field supports ion transport, an additional electrostatic effect has to be taken into account when cations and anions move along a concentration gradient. If the diffusion coefficients of the two ion types differ from each other, diffusion potentials become effective. The smaller ion exhibits a larger mobility and moves ahead. This results in a separation of positive and negative ion charge and thereby in a potential drop along an emerging phase boundary. Due to the resulting electrostatic field ions with higher mobility are retained, whereas the counter ion transport proceeds accelerated. At steady state conditions both ion types move at same speed and a diffusion potential $\Delta\phi_{\text{Diff}}$ results [56]. The thermodynamic driving force to overcome the diffusion potential drop ΔG_{Diff} can be calculated by

$$\Delta G_{\text{Diff}} = -z \cdot F \cdot \Delta\phi_{\text{Diff}}$$

(z : charge number of the ions), and ΔG_{Diff} can be described as the sum of the chemical potential changes $\delta\mu$ of all involved ion species between inner and outer boundary of the diffusion layer [56]. In most cases such diffusion potentials are distinctly smaller than e.g. the potential difference between the electrodes of a galvanic cell. However, they may not be generally neglected if ion transport kinetics at polymer/oxide/metal interfaces are investigated, because the interfacial mobility of cations and anions may differ more than in bulk solution [59].

If this is due to a preferential interaction of positively or negatively charged ions with the metal oxide (preferential adsorption etc.) or with functional groups of the macromolecular network (complexation etc.), ion transport proceeds along electrified interfaces. An electric double layer will be present on the oxide surface of the metal substrate as well as at any boundary between aqueous and organic phase. Therefore, additional electro kinetic mechanisms can be effective which refer to the movement of a liquid phase *along* a solid phase due to an external electric field [55, 56]. They can be best described if the electrolyte saturated polymer/oxide-interface is regarded as an assembly of electrolyte filled capillaries. Ion transport due to cathodic or anodic delamination between an electrolyte covered coating defect and the respective front of corrosive de-adhesion at the adhesive/substrate interface then resembles two electrodes being located at both ends of the capillaries. If ions migrate in an external electric field between cathode and anode, any preferential adsorption of positively or negatively charged species at the capillary walls results in the formation of a diffuse double layer by

oppositely charged ions and a surplus of these oppositely charged ions in solution. The aqueous phase usually exhibits the higher dielectric constant and therefore gets positively charged. Movement of hydrated cations to the cathode will then effectively result in a water flow via the ion hydration shells, a phenomenon known as electro osmosis. Figure 9 provides a schematic overview. It can be shown that the zeta potential ζ , which describes the potential drop across the double layer at the capillary walls, is proportional to the observed (solvent) flow velocity v [55]:

$$\zeta = \frac{\eta \cdot v}{\varepsilon_r \cdot \varepsilon_0 \cdot E}$$

(ε_0 : vacuum permittivity, ε_r : relative dielectric constant of the electrolyte solution). It results in a measurable electro osmotic pressure that destabilizes the adhesive/substrate interface and potentially promotes polymer de-adhesion. Electrolyte flow along the interface can also occur due to a pressure gradient Δp between both ends of the capillaries without externally applied electric polarization. In that case, double layer formation at the capillary walls due to preferential ion adsorption will in turn result in an electric field gradient between both ends of the capillaries, the flow potential U_{flow} :

$$U_{\text{flow}} = \frac{\varepsilon_r \cdot \varepsilon_0 \cdot \Delta p \cdot \zeta}{\eta \cdot \kappa}$$

(κ : electric conductivity of the electrolyte solution) [55]. As a summary, it should be expected that ion transport at polymer/oxide/metal interfaces will be determined by the synergistic interaction of various processes. The contribution of

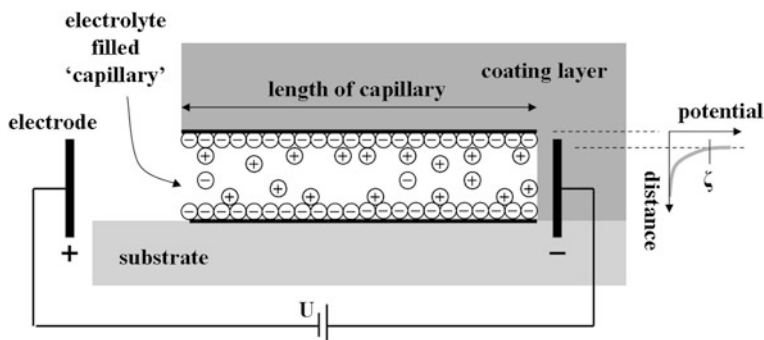


Fig. 9 Schematic illustration of the geometry of a hypothetical capillary at a solid/polymer interface. If this capillary is filled up with aqueous electrolyte, its walls in many cases will get negatively charged due to preferential anion adsorption. This induces a cation surplus in the liquid phase that causes an electro osmotic flow via the hydration shells resulting in an electric field gradient between both ends of the capillary. If an external electric field is generated by polarization with voltage U , electro osmosis in turn will result in a pressure gradient that can destabilize the interface of the sample compound. It was shown that the electro osmotic flow is proportional to the zeta potential ζ , the potential drop across the electric double layer at the capillary walls. (Schematic inspired by [55])

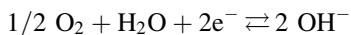
each of these effects to the overall driving force will vary and strongly depend on the structure of the buried interface.

3.2 Corrosive & Cathodic Delamination at Polymer/Oxide/Metal Interfaces

Polymer coatings on metals inhibit electrochemical processes at the substrate surface. Adhesives with adequate barrier properties prevent the access of hydrated ions to the polymer/substrate interface, provide a saturation of adsorption sites at the metal/oxide surface and thereby reduce the maximum interfacial water activity that can be achieved during an exposure to a humid environment. A low interfacial ion concentration will result in a less compact electric double layer at the oxide surface. This is preferred, because a diffuse double layer functions as an additional kinetic barrier for electrochemical processes [42]. As oxidation or reduction process at the oxide surface depend on a discharge or formation of ion species, their passage through a diffuse double layer will consequently occur decelerated and result in reduced interface corrosion under these conditions.

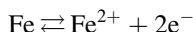
Unfortunately, polymer covered surface areas that surround a coating defect tend to continuously delaminate in humid atmosphere if the defect goes down to the metal substrate and gets into contact with an aerated electrolyte. Already water ingress will weaken the polymer/substrate interface stability, but additional electrochemical processes will even more distinctly accelerate corrosive de-adhesion. They dominate in humid air and on metals such as iron or zinc, which are covered by (semi) conductive oxide structures. Amongst others, the electrochemical properties of the oxide, its solubility at different pH, the oxygen permeability, the adhesion and structure of the organic layer, the type and geometry of an electrolyte filled coating defect as well as the relative humidity of the surrounding atmosphere were highlighted as determinant factors for corrosion mechanisms such as cathodic delamination [60–66].

The resulting electrochemical processes can be interpreted in terms of current–potential-curves (see Fig. 10). On iron substrates oxygen will be reduced in the defect area until the diffusion limiting current density level is achieved or nearly achieved [60, 66, 67]:



This diffusion limiting current density level determines the maximum rate of the electrochemical process. The activation energy for oxygen reduction on electrolyte covered iron is usually low and the reaction rate is consequently that fast that all O_2 molecules passing the compact electric double layer at the oxide surface will be almost immediately reduced. This means that the maximum current density level is determined by the rate at which oxygen diffuses to the electrode.

For charge compensation, iron dissolves as anodic counter reaction, a process that can proceed at a higher rate than oxygen reduction:



Steady state conditions are achieved if the cathodic current density i_{cath} is equal to the anodic current density i_{anod} (see Fig. 10). Oxygen diffusion to the iron oxide surface consequently does not only limit the cathodic process, but also determines the entire kinetics of the galvanic cell. It should be noted that dissolved iron

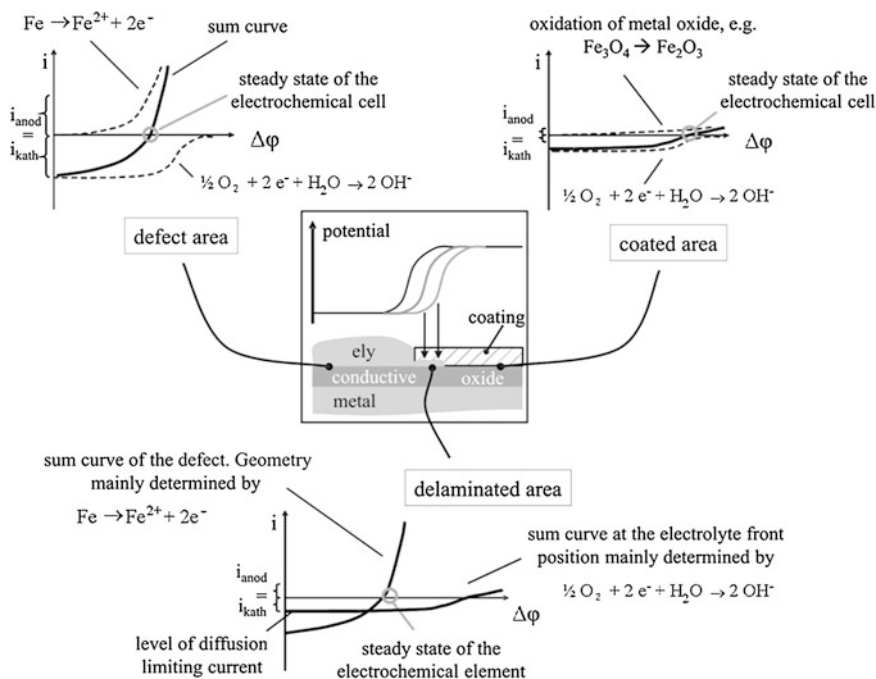
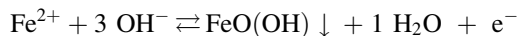
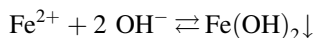


Fig. 10 Illustration of current (i) versus Galvani potential difference ($\Delta\phi$) curves for the description of electrolyte/substrate, polymer/substrate and polymer/electrolyte/substrate interface potentials at a polymer coated iron compound in humid air. Prior to cathodic delamination, two separated galvanic cells are effective: Metal dissolution and oxygen reduction proceed at high rate in the electrolyte ("ely") covered defect. In contrast, O_2 reduction at the intact polymer/substrate interface is strongly inhibited, because metal dissolution is suppressed and only oxide oxidation occurs. Compared to the defect area, this leads to a more anodic (higher) potential at steady state conditions of the galvanic cell and to a characteristic sigmoid potential profile for the interface (see the illustration in the centre of Fig. 10). As soon as the electrolyte penetrates the polymer/oxide/metal interface, a conductive connection between defect and adjacent polymer coated areas is established, the inhibition of the oxygen reduction process is released and the interface potential is shifted down close to the defect potential. The arrows in the central schematic indicate that this results in a lateral displacement of the inflection point in the sigmoid potential profiles with time, which helps to identify the actual electrolyte front position. [Inspired by [59, 60]]

species precipitate within the defect area as ferric or ferrous (oxidic) hydroxides and form red rust:



Initial oxygen reduction can also occur at the intact polymer/oxide/metal interface, because a small amount of O_2 can diffuse through the polymer depending on the barrier properties of its macromolecular network. But due to the non-compact electric double layer at the buried interface, this process is kinetically strongly inhibited. Iron oxide oxidation (for example from FeO or Fe_3O_4 to Fe_2O_3) as anodic counter reaction quickly results in a depletion of $\text{Fe}(0)$ and $\text{Fe}(\text{II})$ donor states within the oxide. This further reduces the achievable anodic maximum current density for oxygen reduction and from the electrochemical point of view has to result in a high anodic overpotential of the galvanic cell at steady state conditions. Consequently, a distinct potential difference between defect area and intact interface will be monitored (see Fig. 10).

The electrolyte at the defect can now penetrate adjacent polymer covered interface areas. Thereby, the kinetic barrier for oxygen reduction at the polymer/oxide/metal interface will be bypassed by an increased anodic metal dissolution in the defect. A direct connection of the two formerly isolated electrochemical cells at defect and intact interface results. The two current–potential-sum curves then determine the interface potential in the delaminated area. Steady state conditions will be achieved at or near the oxygen diffusion limited maximum cathodic current density level. As the polymer functions as a certain barrier for oxygen diffusion, i_{cath} will be relatively small compared to the cathodic current density at the defect. This means that the anodic current density for iron dissolution needs to be only slightly increased to compensate the cathodic O_2 reduction process in the area of interfacial electrolyte ingress. The corrosion potential will be hardly anodically shifted, and because no anodic overpotential is effective in the delaminated area any longer, a potential similar to that one of the defect will be detected. This allows tracking of the cathodic delamination progress by continuous monitoring of the polymer/oxide/metal interface potential. The lateral displacement of the inflection point in the sigmoid potential profile is commonly used as an indicator for the front position of corrosive de-adhesion (see Fig. 10) [60, 66, 67].

The separation of local anode (iron dissolution in the defect) and local cathode (oxygen reduction in the delaminated area) requires a transfer of electrons to the electrolyte front position, which is determined by the electric conductivity of the oxide. A transport of (hydrated) ions along the polymer/oxide/metal interface is required to complete the electric circuit (see Fig. 11). Therefore, cations of the defect electrolyte move towards the front of delamination. They are electrostatically attracted by negatively charged hydroxide ions generated while interfacial oxygen reduction proceeds. Increasing OH^- concentration at the polymer/oxide/metal interface results in a pH of around 13 and passivates the iron substrate.

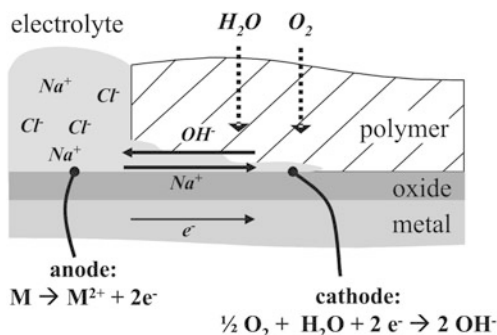
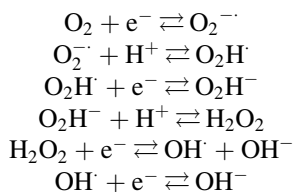


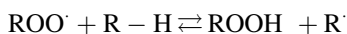
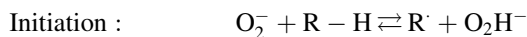
Fig. 11 Schematic illustration of the cathodic delamination mechanism. Electrolyte covering a defect of a polymer coated iron or zinc sheet penetrates the polymer/oxide/metal interface. This is catalysed by a galvanic cell in humid air: Metal (“M”) dissolution occurs at the local anode in the defect, whereas oxygen diffusing through the adhesive layer gets reduced at the buried interface. Hydroxide is generated, which results in an increase of the interfacial pH and a transport of cations from the defect electrolyte towards the front of delamination for charge compensation. Expansion of free volumes at the interface due to electrolyte ingress, structural adjustments of the macromolecular polymer structure and the oxide morphology in alkaline environment as well as oxidative degradation by reactive oxygen species then supports de-adhesion of the coating. The electric circuit is completed by a transfer of electrons between anode and cathode [59]

No interfacial Fe-hydroxide precipitation occurs and OH^- ions are transported to the defect to support charge compensation between the local electrodes. It was observed that the interfacial ion transport is often the slowest process step and therefore rate-determining for cathodic delamination [60, 66, 67].

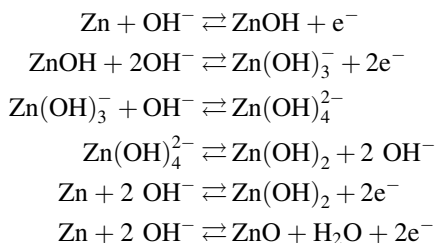
Oxygen reduction at the adhesive/substrate interface promotes an oxidative degradation of the polymer structure. It is expected that this is supported by highly reactive oxygen species, in particular radicals and intermediates evolving during the O_2 reduction process [67]:



A destruction of chemical bonds may be thereby induced, for example via a radical chain reaction (R = hydrocarbon chain) [60, 66, 67].



De-adhesion of the adhesive layer results and its corrosion protective properties are distinctly reduced or even completely lost. The basic mechanisms of corrosive delamination are similar on polymer coated iron and zinc substrates, but additional effects arise from the fact that zinc exhibits amphoteric properties at high pH [68–70]. Oxygen reduction at polymer/zinc/zinc interfaces passivates Zn and results in the formation of zinc hydroxide. However, Zn(OH)_2 tends to dissolve as zincate species, e.g. Zn(OH)_4^{2-} in strongly alkaline solution, which buffers any additional alkalization. This means that a pH value of 13 will not be achieved on polymer coated zinc compounds and that zinc hydroxide can take part in a dissolution/precipitation mechanism in the area of interfacial ion transport [68]:



Distinct thickening of the oxide layer is reported for ongoing delamination at polymer/zinc interfaces. In contrast, additional iron oxide/iron hydroxide growth on polymer coated Fe samples has to occur via solid state diffusion of cations through the already existent oxide structure and is therefore less pronounced. The amphoteric properties of Zn result in another two important consequences for the kinetics of corrosive delamination. First, zinc dissolution at the buried interface is an anodic process and generates additional positive charge which partly ‘neutralizes’ the negative charge resulting from interfacial oxygen reduction and OH^- formation. Less cations of the electrolyte in the defect thereby have to be transported along the polymer/zinc/zinc interface for charge compensation. Moreover, the electrostatic repulsion of anions of the defect electrolyte should be reduced and anion ingress was indeed observed at adhesive/zinc compounds. Second, dissolved zinc species at the interface can react with CO_2 that is present in ambient air and form precipitates of zinc carbonate. This does not only reduce the interfacial pH, but also results in voluminous and white-coloured, gel-like deposits at the interface which promote de-adhesion of the polymer layer. In contrast, iron or low alloyed steel maintains a shiny surface in the delaminated area [59, 60, 66–70].

It has been noted above that the progress of cathodic delamination and interfacial ion transport can be adequately tracked by monitoring of interface potentials. In that context, especially the Scanning Kelvin Probe (SKP) has been established as a method for non-destructive measurements at buried polymer/oxide/metal interface compounds [71–81]. A SKP utilizes a metallic needle that vibrates above a conductive sample surface with the needle tip, the substrate surface directly beneath and the air in between needle and sample forming a parallel-plate capacitor. Thereby, any ad- and desorption, ion ingress, dissolution or structural rearrangement processes at the sample surface will cause an

adjustment of the charging condition of the capacitor. This will induce a current in the external electric circuit of the SKP, which is translated into a change of the Volta potential of the investigated substrate. It was shown that the recorded potentials can be referenced to the standard hydrogen electrode after calibration with a redox couple (e.g. an electrolyte covered metal) of known potential. To investigate the progress of corrosive delamination with time, continuous scanning of the SKP needle along the polymer/oxide/metal interface is required [71–81].

Figure 12 presents an example of potential distributions typically recorded on epoxy covered iron (shown in Fig. 12a, c) and along an epoxy coated iron/zinc transition (shown in Fig. 12b, d). Ion ingress started from a coating defect located at the left, but outside of the scanned area which was filled up with 0.5 molar NaCl solution. During the first stage of the experiment interface potentials were analysed in humid nitrogen atmosphere with an oxygen partial pressure of less than 1 mbar (see Fig. 12a, b). A transport of hydrated ions along the polymer/oxide/metal interface was observed in the coated iron area. It became manifest in a proceeding front that caused a potential shift from -200 to -250 mV_{SHE} (SHE: Standard

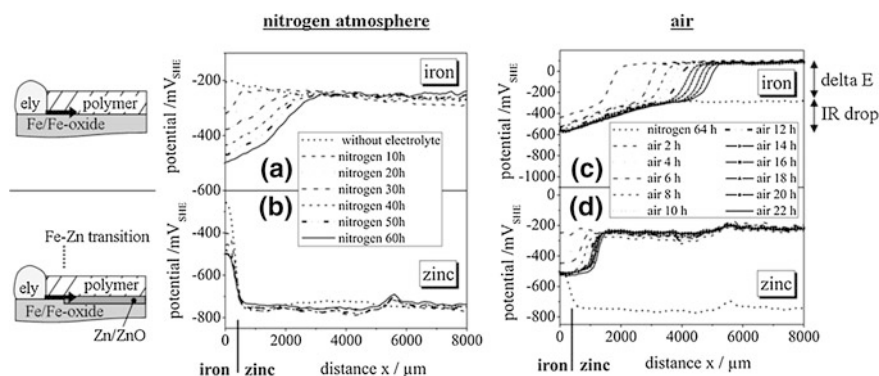


Fig. 12 Study of interfacial ion transport along epoxy/iron and epoxy/zinc interfaces starting in humid nitrogen atmosphere with an oxygen partial pressure below 1 mbar (see Fig. 12a, b). After 64 h, the atmosphere was changed to humid air (see Fig. 12c, d). The schematics at the left provide a cross section view of the sample geometries. In Fig. 12a, c, an epoxy coated iron sample with an artificially prepared, electrolyte (“ely”) covered coating defect was investigated. In Fig. 12b, d, ion transport first proceeded along an epoxy/iron interface, then along an epoxy/zinc interface. The Fe-Zn-transition is located at around $x = 400$ μm . The progress of interfacial ion ingress was tracked by continuous scanning along the sample surfaces with a Kelvin Probe and by monitoring of the polymer/substrate interface potential. The diagrams present the resulting potential profiles for transport processes that proceed from the left to the right. DeltaE indicates the potential difference between intact polymer/metal interface sections and corroded areas. It reflects the electrochemical driving force for cathodic delamination, whereas the IR drop is related to the electrolyte resistance that has to be overcome for ion migration between the local anode in the defect and the electrolyte front position. Figure 12 shows that interfacial ion transport proceeds accelerated in humid air and that a transport cannot be observed on zinc substrates for inhibited interfacial oxygen reduction kinetics (Adapted from Ref. [34], Copyright 2009, with permission from Elsevier)

Hydrogen Electrode scale) to the level of actively corroding iron in the defect with an interface potential of about $-500 \text{ mV}_{\text{SHE}}$. The polymer coated zinc area did not show any potential changes. No ion transport occurred beyond the iron/zinc transition. After the recipient was flushed with humid air the potential levels between defect and zinc inverted. Figure 12d shows that the potential of the epoxy coated zinc area then is higher than the defect potential and corrosive delamination started, but proceeded more slowly than on iron (see Fig. 12c). After 22 h of exposure to humid air, the electrolyte front is located at approximately $x = 4,900 \text{ }\mu\text{m}$ on iron and approximately $x = 1,200 \text{ }\mu\text{m}$ on the iron/zinc sample, which in fact refers to an effective transport distance of not more than $800 \text{ }\mu\text{m}$ along the epoxy coated zinc interface [34]. Several conclusions about interfacial ion transport mechanisms can be drawn based on the data presented in Fig. 12 and on additional measurements reported in literature:

- Ion transport at polymer coated iron, steel, zinc or copper samples proceeds at a relevant rate if the potential of the intact polymer/oxide/metal interface is higher than the defect potential [60, 66, 67]. The potential difference ΔE between both areas reflects the electrochemical driving force for interfacial ion ingress. Fig. 12c, d confirm that accelerated ion transport is commonly observed if ΔE is increased. No corrosive delamination is detected if the potential levels are inverted, which means that the potential of the intact interface is lower than the defect potential. This also shows that interfacial ion transport cannot be initiated without electrochemical driving force, because macroscopically relevant ion diffusion along polymer coated zinc surfaces is *not* observed in an atmosphere of distinctly reduced oxygen partial pressure [35].
- The interface potential increases linearly between defect and the electrolyte front position. This IR drop is illustrated in Fig. 12c and reflects the ohmic electrolyte resistance between the local electrodes of the galvanic cell that has to be overcome for Na^+ transport along the epoxy/ironoxide/iron interface [60, 66, 67].
- Reduced oxygen partial pressure in the atmosphere lowers the polymer/substrate interface potential, decelerates interfacial oxygen reduction kinetics and reduces the transport rate of hydrated Na^+ ions along the interface (see Fig. 12a and compare with Fig. 12c) [34, 35].

It should be noted that the progress of cathodic delamination was found to decrease with increasing hydrodynamic radii of the cations of the defect electrolyte, whereas the size of the hydrated anions did not have any influence on the process kinetics. Additionally, the kinetics of interfacial ion transport were subject to a square-root-of-time dependency. This allowed for the calculation of at least ‘formal’ coefficients for cation transport based on the concept of Fickian diffusion [59, 60, 66, 67].

Moreover, some analogies were drawn between corrosive delamination at polymer coated iron or zinc substrates and droplet spreading observed on uncoated Fe and Zn surfaces. The concept is based on the effects of interface tension and electro kinetics. It may explain why no ion transport is observed on polymer coated

zinc in humid atmospheres of reduced oxygen partial pressure and why even porous adhesive layers do not enforce ion ingress under these conditions [34, 35].

If a droplet of NaCl solution is placed on a zinc sheet in humid air, it will spread with time (see Fig. 13a, b). Figure 13c, d present maps illustrating the elemental distribution on the metal surface resulting from that process. It reveals that chloride is solely observed in the area of the original droplet, whereas sodium can only be detected in the electrolyte spreading zone. This finding is similar to what has to be expected from corrosive delamination at buried polymer/oxide/metal interfaces which starts from an electrolyte covered defect in the coating. Figure 14a schematically describes the basic mechanism on zinc for an atmosphere free of carbon dioxide. A strong alkalisation of the liquid phase in the spreading zone was observed due to oxygen reduction processes in the periphery of the droplet/at the electrolyte front and it was detected that spreading accelerates if the pH is increased [82–84].

The wettability of the zinc oxide surface by electrolyte films is equivalent to the energy that has to be invested to generate an area normalised surface during an isothermal and isobaric process. The surface energy of a solid can be calculated based on measurements of the contact angle θ , which is defined as angle between the vectors of liquid/gas interface tension σ_{lg} and solid/liquid interface tension σ_{sl}

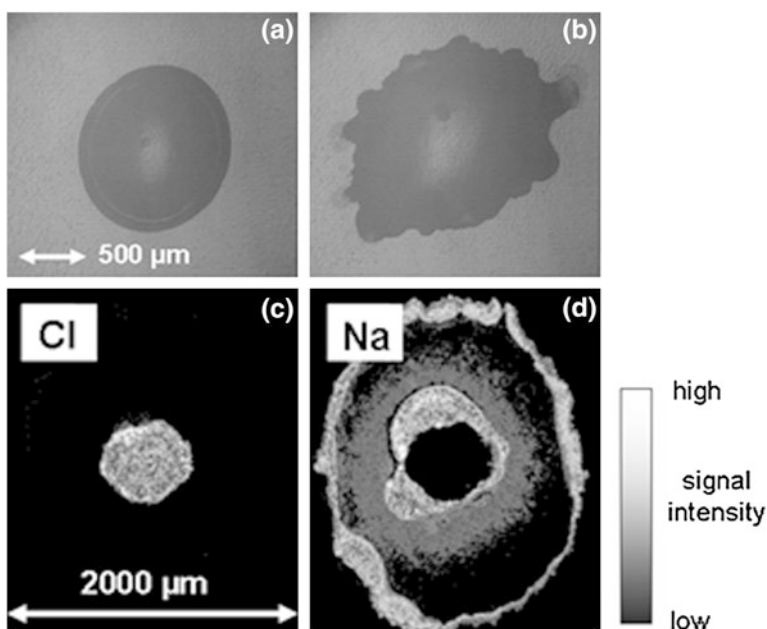


Fig. 13 Electrolyte droplet spreading on zinc in humid air. **a** Photo taken after one hour of droplet spreading, **b** photo taken after two hours. **c** and **d**): Elemental distribution resulting from spreading of a droplet of NaCl solution. Chloride is only detectable in the area of the droplet, whereas sodium in contrast is only observed in the spreading zone. (Modified from Ref. [82], Copyright 2008 and modified from Ref. [83], Copyright 2002, with permission from Elsevier)

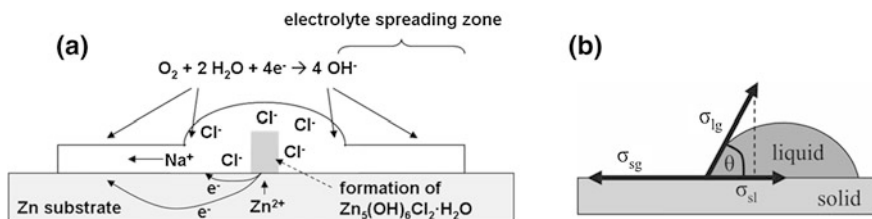


Fig. 14 **a** Schematic illustration of fundamental processes resulting in electro kinetic droplet spreading on zinc in humid, CO_2 -free air (Adapted from Ref. [82], Copyright 2008, with permission from Elsevier). **b** Illustration of contact angle θ for the solid/liquid (sl), solid/gas (sg) and liquid/gas (lg) interface tensions σ [55, 59]

(Young's equation; σ_{sg} : solid/gas interface tension; see also Fig. 15b) [55, 56, 85, 86]:

$$\sigma_{sg} = \sigma_{sl} + \sigma_{lg} \cdot \cos \theta$$

Gibb's Free Energy quantifies the thermodynamic driving force for liquid spreading on an oxide-covered zinc surface:

$$-\Delta G \sim (\sigma_{sg} - \sigma_{sl} - \sigma_{lg}) \quad (3)$$

The process will occur spontaneously if the spreading coefficient, which is reflected by the expression in the parenthesis of equation 3, is positive. σ_{sg} and σ_{lg} will hardly be affected or change during droplet spreading, but a reduction of σ_{sl} will effectively promote the process. The oxide/electrolyte interface tension is maximised at the isoelectric point of ZnO, which ranges around pH 9. It decreases if the pH increases above this value. This is achieved by oxygen reduction in the periphery of the electrolyte droplet, which results in the generation of OH^- and a negatively charged substrate surface. Liquid flow towards the outer parts of the droplet will consequently destabilize its edges. If the oxygen partial pressure in the atmosphere is too low to induce relevant O_2 reduction kinetics, stable droplets and no spreading has to be expected and no interfacial ion transport is observed even at polymer/zinc oxide/zinc interfaces [82, 84].

3.3 Anodic Delamination at Polymer/Oxide/Metal Interfaces

Anodic undermining of polymer layers on non-conducting oxide surfaces and insulating inorganic films usually dominates during the exposure of painted metal compounds to an atmosphere with a relative humidity of typically at or above 80 %. It is also observed when the metal is covered by a barrier layer that strongly inhibits the access of water and oxygen to the substrate material. Anodic delamination consequently often occurs as filiform corrosion on Al-alloys and as bondline corrosion of adhesively bonded metals or composites [87–90].

Anodic disbondment is characterised by net anodic current densities ($i_c < i_a$) at the front of delamination adjacent to interface sections for which net cathodic current densities ($i_c > i_a$) are detected. This causes a transport of excess electrons from the anodic to the cathodic region, specific pH values at the delamination front, defect and delaminated area as well as a pH- and electrolyte-dependent formation of corrosion products (see Fig. 15). Anodic disbondment of adhesives on zinc alloy coated steel and filiform corrosion on Al-alloys are technically most important and will be consequently discussed more in detail.

In contrast to the characteristics of cathodic delamination described above, SKP-profiles that are recorded on polymer coated and low-conductive Zn-Al layers on steel exhibit more negative potentials at the front of undermining than close to the defect (see Fig. 16) [92]. Simonkolleite can be detected in the delaminated zone while zinc oxides and zincates form in the cathodic region close to the defect. This anodic undermining was attributed to the specific properties of the polymer film that functions as an effective barrier for oxygen diffusion. It ensures constantly low O_2 concentrations at the buried interface underneath the coating. Similar to the mechanisms of crevice corrosion, anodic dissolution of the base material at the front of delamination occurs as long as de-adhesion or blistering of the polymer does not significantly reduce the barrier properties at the interface against electrolyte, water and oxygen ingress [93].

Growing threadlike filaments on polymer coated, insulating oxide surfaces such as MgO on Mg or Al_2O_3 on Al are characteristic for filiform corrosion. They are observed in not too humid atmosphere and their growth is promoted by the

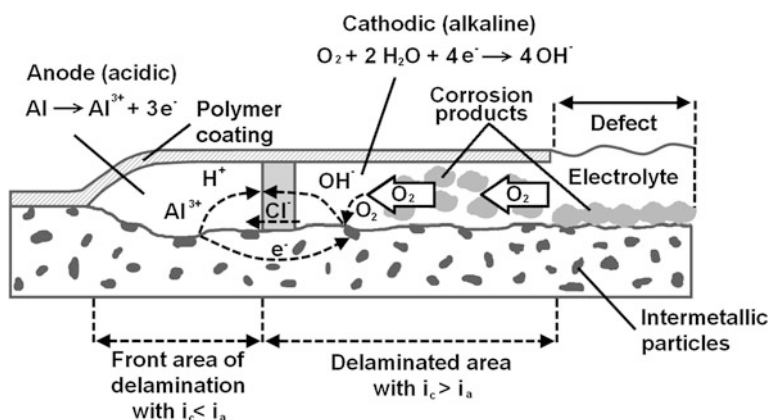


Fig. 15 Schematic illustration of the anodic delamination mechanism at a polymer coated Al-alloy. Anodic undermining is characterised by the formation of a differential aeration cell and by oxidative dissolution of the metal at the head of the filament. In the tail region, O_2 reduction is induced and results in the formation of voluminous corrosion products. For charge compensation, anions of the defect electrolyte are transported to the front of delamination. The entire process is strongly supported by the presence of local conducting sites such as intermetallic particles in the aluminium matrix. In general, acidic pH will be detected at the filament head, whereas an alkaline environment has to be expected in the filament tail (figure adapted from Ref. [63, 91])

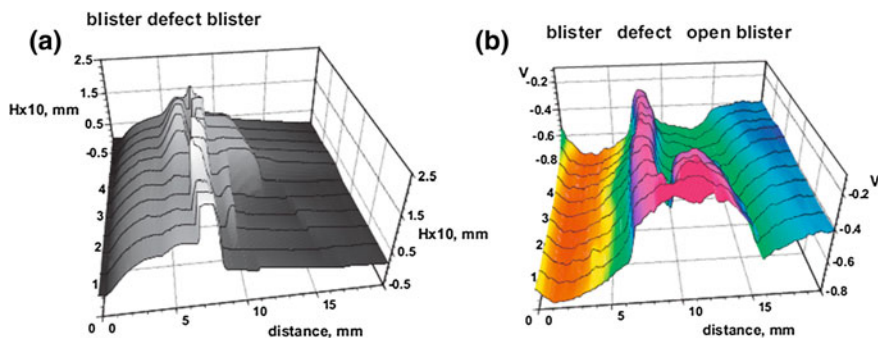


Fig. 16 **a** Topography map and **b** potential distribution for a blister beneath a polymer coating (*on the left*), of a defect zone (*in the centre*) and of an open blister (*on the right*). The measurements were performed on a polymer covered Zn-Al substrate in humid air. As the macromolecular film functions as an effective barrier for oxygen diffusion, no cathodic delamination, but anodic undermining processes are observed at the buried interface. As a result, the potentials at the front of delamination are more negative than those detected close to the defect (Adapted from Ref. [92], Copyright 2012, with permission from Elsevier)

presence of soluble anionic species in coating defects, for example by chloride [67, 94–96]. Relevant conditions for the initiation of filiform corrosion on various metals including aluminium, iron, magnesium and even zinc-coated steel, silver and gold have been studied in detail [61, 77, 97–106]. The filaments propagate by an anodic undermining process, which arises from a differential aeration cell within the filament head. As a consequence, the metal substrate is oxidized at the head front (anode) and oxygen is reduced in the vicinity of the head–tail junction (cathode) [107]. Between anode and cathode, a potential gradient is established that enforces a migration of anions to the front of delamination and of cations to the coating defect. On aluminium substrates, an exceptionally low pH and the oxygen deficiency at the front edge of the filament thread can additionally result in a secondary cathodic hydrogen evolution.

During the initiation period, aluminium oxide dissolves in a coating defect, supported by the presence of chloride [108]. This weakens the oxide layer and delamination of the adjacent polymer coating is promoted due to combined mechanical and electrochemical de-adhesion [109]. In a second step, metal dissolution at the polymer/metal interface results in the formation of a small crevice so that the electrolyte solution can penetrate the coated region. This, in turn, promotes chloride induced weakening of the polymer covered oxide layer and finally results in anodic dissolution of the base material underneath the coating. The corresponding cathode will be primarily located close to the defect, but corrosion products formed by released metal ions and artifacts evolving from oxygen reduction then cause the formation of an occluded cell [110]. The exact anolyte and catholyte compositions are not clear yet, but very low pH values of 1–2 [111–113], hydrogen evolution and high chloride concentrations [112] at the outermost filament tips were reported.

Figure 17 presents a Scanning Kelvin Probe potential- and topography-map. They were simultaneously recorded on a filiform filament that evolved on an epoxy coated aluminium specimen [61, 102, 107]. The graphs show that the potential at the filament tail is about 150 mV higher than that of the surrounding polymer coated aluminium matrix. This indicates the formation of aluminium-oxide/-hydroxide corrosion products and points at processes such as oxygen reduction in the filament tail. The active part of the filament head, where the anodic reaction of active metal dissolution takes place, exhibits a potential of about 500 mV lower than that of the intact sample surface. Direct comparison of potential and topographic maps reveals that a larger surface area is affected by filiform corrosion induced potential shifts than by topographic changes due to deformation and lifting of the epoxy film. This confirms that the polymer/metal interface has to be electrochemically degraded before blistering of the macro-molecular coating layer is observed. Moreover, Fig. 17 shows that the anodically

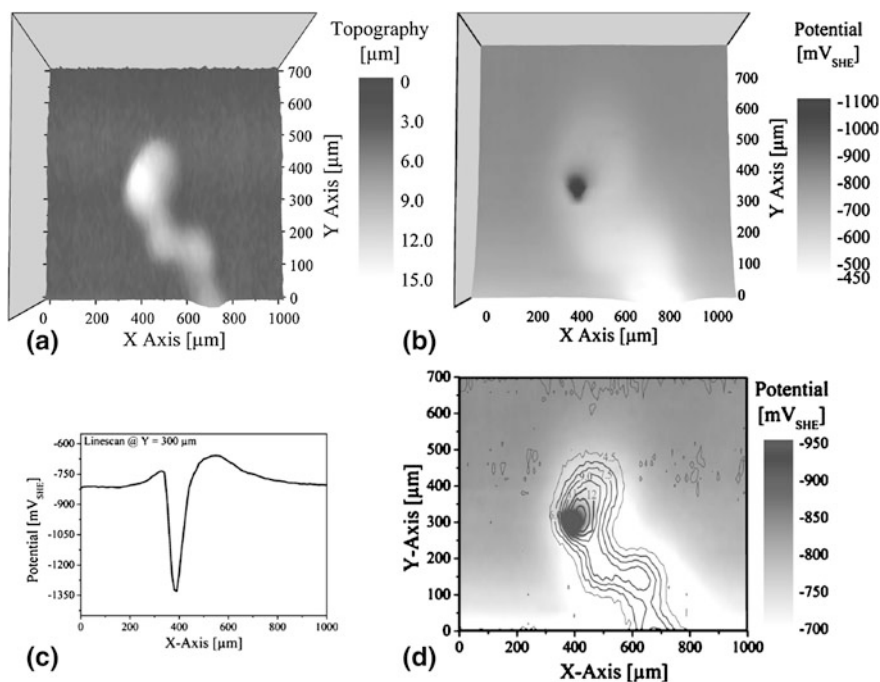


Fig. 17 Height-regulated SKP (HR-SKP) measurement of a single filiform thread on an organically coated aluminium substrate under active filiform corrosion conditions: **a** HR-SKP topography map. **b** HR-SKP potential map. Higher potentials are detected in the filament tail compared to surrounding intact areas. This indicates the formation of aluminium-oxide/-hydroxide corrosion products via oxygen reduction processes. Distinctly lower potentials are observed in the filament head due to anodic metal dissolution (Reprinted with permission from Ref. [81], Copyright 2005, The Electrochemical Society)

active area is confined to a rather small region at the left border of the filament head and not located in the center or across the whole area of the head.

It should be noted that the kinetics of filiform corrosion are strongly dependent on the presence of intermetallic particles in commercially relevant aluminium alloys. These intermetallics function as hot spots for the propagation of the filament thread, a process that can be specifically investigated for example by scanning Kelvin Probe force microscopy [87, 114–117].

4 Conclusions

The design of water- and electrolyte-resistant adhesive joints for humid environments remains a challenge due to the complexity of polymer/metal interface structures. The morphology and chemical properties of metal oxides, barrier properties of macromolecular networks as well as type and nature of chemical interactions between the polymer film and the oxide surface have to be specifically tailored to achieve flexible systems that can dynamically adjust to varying environmental conditions. Some basic facts have to be taken into account based on recent progress in the field of corrosion and adhesion research:

- Water molecules form a highly mobile hydrogen bonding network which lowers the adhesion forces at polymer/oxide interfaces.
- Hydrated ions can be transported along polymer/oxide interfaces in water rich environments.
- The conductivity of the oxide and the interfacial water activity determine corrosive de-adhesion processes at the polymer/metal interface. Conductive oxides and high H₂O concentrations result in cathodic delamination whereas insulating oxides and embedded local conducting sites ('hot spots of electrochemical reactivity') promote anodic de-adhesion.

If externally applied mechanical forces are not sufficient to break interfacial bonds, de-adhesion of polymers from metal substrates results from the interaction of water accumulation at the adhesive/metal interface, from the ingress of hydrated ions as well as from electron and ion transfer reactions across the interface. Therefore, state-of-the-art surface technology approaches generally aim at the development of adhesives with improved covalent and coordinative bonding between the macromolecular phase and the metal to also suppress electrochemically determined corrosion processes.

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