Ultrathin Chemisorbed Polymer Coatings: Corrosion Protection and Nanostructuring of ZnO

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To my beloved parents,
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Zusammenfassung


In dieser Arbeit wurde gezeigt, dass die Grenzflächenstabilität zwischen Metall und Polymer aber auch die Metalloxid Eigenschaften einen entschiedenen Einfluss auf die Delamination von Polymerbeschichtungen haben. Außerdem wurde dargelegt, dass die eigentlich unerwünschte Korrosion von Metallen zur großflächigen Herstellung von Zinkoxid Nanostäbchen genutzt werden kann.
Abstract

The primary aim of this work is to provide better understanding of adhesion properties at polymer/metal interface as well as the deadhesion process of polymer coatings from metal surfaces due to cathodic delamination. Ultra-thin Poly(methylmethacrylate) [PMMA] and poly(styrene) [PS] coatings that were covalently attached to the zinc substrate were synthesized. The stability of these coatings against cathodic delamination was characterized using scanning Kelvin probe (SKP). The results indicate that covalently bound polymer coatings to metal substrate shows reduction in rate of cathodic delamination by a factor of $\sim 10$. Moreover, adding a cross-linker to a polymer coating further slows down delamination, with another factor of $\sim 10$. Moreover, delamination rates are reaction-controlled for the system investigated here, as shown by linear time dependence.

The other area of interest in this work was to study the corrosion products formed at the metal surface as a result of deadhesion of polymer coating due to cathodic delamination. The analysis of corrosion products shows the formation of ZnO nanorods at the surface of the metal. Hence, this study also provides a very simplified and economically feasible route to fabricate ZnO nanorods via a tailored corrosion process. These ZnO nanorods act as photocatalysts for aerobic photooxidation of organic dye methyl orange under illumination with red light, which is normally accessible only to narrow band semiconductors. Furthermore, the growth of these ZnO nanords was studied by in situ Raman experiments. The obtained in situ data reveals that at initial stages of synthesis, preferentially defect rich ZnO grows while in the later stages, wurtzite ZnO growth becomes more pronounced.

In the present work, the important factors in adhesion and disbonding processes of covalently bound polymer coatings has been evaluated. It is shown that the interfacial chemistry at polymer metal interface and the properties of oxide itself strongly influences the delamination properties of a polymer coating. Moreover, it was demonstrated that usually unwanted corrosion process can be utilized to produce large areas of ZnO nanorods.
Contents

1 Introduction ................................. 1
  1.1 Corrosion of metals ..................... 1
  1.2 Polymer coatings for corrosion protection .......... 2
    1.2.1 Adhesion at polymer/metal interface .......... 3
  1.3 Deadhesion of polymer coatings from metallic substrates ....... 6
    1.3.1 Cathodic delamination .................... 6
    1.3.2 Anodic delamination ..................... 7
    1.3.3 Migration of species through polymer coatings ....... 8
  1.4 Corrosion products ....................... 10
    1.4.1 Corrosion products of zinc in aqueous solutions ...... 10
    1.4.2 Corrosion process for fabrication of Zn(O) nanostructures ... 12

2 Aims and Concepts ......................... 15
  2.1 Motivation and aims of the work .......... 15
  2.2 Approach ................................ 17
    2.2.1 Surface of interest .................... 17
    2.2.2 Synthesis of chemisorbed polymer coatings ....... 17
    2.2.3 Model corrosion experiments ............... 19
    2.2.4 Study of corrosion products ............... 20
  2.3 Thesis outline .......................... 20

3 Experimental Techniques ................. 23
  3.1 Analytical techniques for characterization of surface modification ... 23
    3.1.1 Infrared (IR) spectroscopy ................ 23
    3.1.2 X-ray photoelectron spectroscopy (XPS) ......... 23
    3.1.3 Time-of-Flight secondary ion mass spectrometry (TOF-SIMS) ... 24
    3.1.4 UV/Vis spectroscopy ..................... 24
    3.1.5 Ellipsometry ............................ 25
  3.2 Analytical techniques for characterization of corrosion behavior ...... 25
    3.2.1 Scanning Kelvin probe (SKP) ............... 25
    3.2.2 Linear polarization ...................... 26
    3.2.3 Electrochemical impedance spectroscopy (EIS) ....... 27
  3.3 Analytical techniques for characterization of corrosion products ....... 28
    3.3.1 Electron microscopy ..................... 28
3.3.2 Atomic force microscopy (AFM) ........................................... 28
3.3.3 X-ray diffraction (XRD) .................................................. 29
3.3.4 Raman spectroscopy ....................................................... 29
3.4 Sample preparation .......................................................... 29
3.4.1 Materials ................................................................. 29
3.4.2 Surface modification ...................................................... 30
3.4.3 Synthesis of ZnO nanostructures .......................................... 31
3.4.4 Electrochemical evaluation of stability of polymer coatings ............ 32
3.4.5 Photocatalytic decomposition of methyl orange (MO) .................. 32

4 PMMA model coatings bound via organosilanes 35
4.1 Introduction ................................................................. 35
4.2 Results and discussion .................................................... 36
4.2.1 Surface modification ...................................................... 36
4.2.2 Model corrosion experiments ............................................ 40
4.2.3 Discussion of the chemistry of cathodic delamination .................. 45
4.3 Summary ................................................................. 47

5 PS model coatings bound via organosilanes 49
5.1 Introduction ................................................................. 49
5.2 Results and discussion .................................................... 50
5.2.1 Synthesis of polymer coatings .......................................... 50
5.2.2 Model corrosion experiments ............................................ 53
5.3 Summary ................................................................. 55

6 PMMA model coatings bound via ester linkage 57
6.1 Introduction ................................................................. 57
6.2 Results and discussion .................................................... 58
6.2.1 Surface modification ...................................................... 58
6.2.2 Model corrosion experiments ............................................ 61
6.3 Summary ................................................................. 64

7 Comprehensive discussion on cathodic delamination 65

8 Delamination kinetics on ZnO 69
8.1 Introduction ................................................................. 69
8.2 Results ................................................................. 70
8.3 Summary ................................................................. 75

9 Growth of ZnO nanorods 77
9.1 Introduction ................................................................. 77
9.2 Results ................................................................. 78
9.2.1 Structure and morphology ............................................. 78
9.2.2 Light absorption and photocatalytic activity ........................... 81
Contents

9.3 Summary ......................................................... 85

10 In situ Raman studies on the growth of ZnO nanorods 87
10.1 Experimental details ............................................. 88
10.1.1 Materials .................................................. 88
10.1.2 Synthesis of ZnO nanostructures ........................... 89
10.1.3 Analytical techniques ...................................... 89
10.2 Results and discussion .............................. 88
10.2.1 Change in surface morphology during growth .......... 93
10.2.2 Effect of electrolyte concentration ....................... 94
10.2.3 Optical properties of ZnO nanorods ....................... 95
10.3 Summary ....................................................... 98

11 Summary and Outlook 99
11.1 Summary ....................................................... 99
11.2 Outlook .......................................................... 101

Appendix 125
1 List of Figures ..................................................... 127
2 List of Tables ....................................................... 129
3 Abbreviations ..................................................... 130
4 List of publications till November 2014 ..................... 131
5 Conference oral presentations & posters .................... 131
6 CV .................................................. 133
Chapter 1: Introduction

Corrosion is a common problem which we are facing for over a hundred years. It is a naturally occurring phenomenon termed as deterioration of a material and its properties due to reaction with its surrounding environment. Like other natural hazards, corrosion can lead to dangerous and expensive damages in almost every areas from commodity products like plumbing systems, sewer utility lines to high-tech products like airplanes, rockets etc. Several years ago, a study conducted by U.S. Federal Highway Administration (FHWA) showed that the total estimated cost of damages and prevention of corrosion is approximately 3.1% of the nations gross domestic product (GDP)\(^1\). This study points to the fact that corrosion not only leads to loss of desired properties but also has huge economic costs that are needed for the repairs or complete replacement of a corroded material. However, the figures mentioned above are only the direct economic costs of corrosion. The indirect costs (such as plant down time, loss of product, loss of efficiency etc) resulting from actual or possible corrosion can be even more but they are difficult to evaluate\(^2\)[pp. 55].

In particular, corrosion of metals is of significant research interest due to its economic and commercial importance. Hence, several methods have been developed by material scientist and engineers which are time proven to minimize/prevent corrosion. These methods include corrosion protection by metallic coatings\(^3\), conversion coatings\(^4,5\), with the aid of inhibitors\(^6,7\), self-healing coatings\(^8-10\), and by organic coatings\(^11,12\). In the following chapters of this work, corrosion of metals and their protection by organic coatings will be discussed in detail. In particular, aliphatic (PMMA) and aromatic (PS) polymer coatings having silane and ester linkage with zinc substrate has been synthesized and their resistance against cathodic delamination has been investigated. Moreover, corrosion products formed on top of the surface as a result of cathodic delamination is another area of interest that would be discussed in detail.

1.1 Corrosion of metals

Metallic corrosion has been the subject of many research articles and text books\(^13-15\). Metallic corrosion is an electrochemical process which involves transfer of a charge. Hence, it is useful to first briefly discuss the electrochemistry of corrosion before continuing to methods of corrosion protection. Metallic corrosion is an heteroge-
Chapter 1. Introduction

Inertous electrochemical reaction that usually occurs at metal-environment interface. If we consider a corrosion of metal in an aqueous solution (which usually contains dissolved ionic species), they result in oxidation of metal leading to the formation of ionic species that takes electrons which comes from the metal. As an example a generic oxidation reaction of metal (M) is shown below:

\[ M \rightarrow M^{z+} + ze^- \]  

(1.1)

However, the above reaction also called half reaction is an incomplete reaction as the free electrons formed due to oxidation of metal must be consumed. These liberated electrons are consumed eventually by a reduction reaction which occurs on the same surface\textsuperscript{14} [pp.3-8]. A common example of reduction reactions are hydrogen evolution and oxygen reduction, which are shown below.

\[ 2 H^+ + 2 e^- \rightarrow H_2 \]  

(1.2)

\[ O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^- \]  

(1.3)

\[ O_2 + 4 H^+ + 4 e^- \rightarrow H_2 + 2 OH^- \]  

(1.4)

The location where oxidation of metal takes place is termed as anode, while the place where reduction reaction takes place is called cathode and these are the electrodes.

1.2 Polymer coatings for corrosion protection

Polymers are a class of synthetic materials that consist of small molecules (monomer) linked together through a covalent bonding forming long chain molecules called macromolecules\textsuperscript{16}. Due to huge diversity and ease of modification in the properties of polymers, they are nearly used in all of our current commodity and industrial products. One of the important application area of polymers is there use as coatings to protect metals against corrosion. Moreover, they are also responsible for improved surface properties like roughness and aesthetic appearance. Polymers prevent the corrosion of metals by isolating them from the corrosive environment which leads to suppression of both anodic dissolution of metal and the corresponding cathodic reaction.

Polymers can be synthesized in a number of ways such as addition polymerization and condensation polymerization. Free radical polymerization is one type of addition polymerization that is widely used to synthesize commercial polymers. In free radical polymerization, monomers add one by one to an active side of growing chain. Free radical polymerization reaction mainly consist of three steps i.e. initiation, propagation, and termination\textsuperscript{17}. In the initiation step, an initiator (such as AIBN, BPO) decomposes into free radicals either by heating or shining light on them (depending on the type of initiator used) in presence of monomers. The monomer consist of unsaturated carbon-carbon double bond that reacts with an unpaired electrons in a radical. In this reaction, the active center of the radical 'grabs'
1.2. Polymer coatings for corrosion protection

One of the electrons from the unsaturated bond of the monomer, leading to a new active center at the either end of the chain. The next step is a propagation step, where at the active end of the chain new monomers are connected and continues to grow. Finally the growth of polymer chains are stopped by a termination reaction where two active ends of growing chains are joined together or as a result of hydrogen extraction. The steps of free radical polymerization are shown schematically in Figure 1.1.

![Figure 1.1: Schematic representation of steps in classical free radical polymerization.](image)

1.2.1 Adhesion at polymer/metal interface

Polymer coatings are applied to inorganic substrates as a liquid solution, primarily by dip coating, spray coating, and brushing etc. After the coating process, liquid phase is evaporated at room temperature or by heating at higher temperatures, leaving a dry polymer coating covering the metal surface. However, the factor which plays a more crucial role in corrosion protection of metals is the barrier properties of a polymer coating and adhesion at polymer/metal interface. Polymer coatings mainly interact with metal/oxide surfaces in three ways:

a) mechanical interlocking, where two surfaces interact via interlocking due to roughness,
b) by physisorption, where coating interacts with the inorganic substrate via physical forces like van der Waals forces and dispersion forces (London),

c) by chemisorption, where the polymer coating makes a covalent bond with the substrate.

Mechanical interlocking is usually observed for rough surfaces where polymer can go in to the cavities and attach well to the surface. Recently, it has been shown that increase in surface roughness leads to better protection against cathodic delamination of epoxy coated steel. It has been well established in the literature that acid-base interactions between polymer/metal interface plays a major role in adhesion forces. Moreover, it has been shown that when molecular interaction dominates, it results from the chemical bonding between reactive species on polymer and the substrate or due to molecular interactions between these two.

Wetting of the surface plays an important role because for any type of interaction, the coating and substrate must be very close to each other. This can be achieved by wetting of the surface which is determined by the surface tension of substrate and a coating material. To achieve complete wetting, the substrate should have higher surface energy than the coating material. This can be expressed in mathematical term as a spreading coefficient $S$, which is given by the difference in the surface energy of covered and uncovered surface.

\[
S = \gamma_{SV} - (\gamma_{Sl} + \gamma_{lV})
\]

where $\gamma_{SV}$ and $\gamma_{Sl}$ are the solid-liquid and solid-air surface energies, respectively, while $\gamma_{lV}$ is the interfacial energy of the liquid. In order to have complete wetting of the surface, the value of spreading coefficient should be positive. Higher values of $S$ indicates that the surface would wet more rapidly. The adhesion strength between substrate and a coating material can be quantified by work of adhesion. Work of adhesion ($W_a$) is defined as the force applied to separate the interface per unit area.

\[
W_a = \gamma_\alpha + \gamma_\beta - \gamma_{\alpha\beta}
\]

where, $\gamma_\alpha$ and $\gamma_\beta$ are the surface tension of substrate and coating material, respectively, while $\gamma_{\alpha\beta}$ is the interfacial tension between substrate and coating material. Oxide surfaces can interact in various ways with different functional groups of the coating. Either the surface hydroxyl groups of oxide or the functional group of organic molecule can act as the acid (as proton donor is Bronsted sense or the electron acceptor in lewis sense) or as a base (proton acceptor or electron donor). The bond between the functional groups of the oxide surface and a polymer coating can range from fully covalent bonding to very weak ionic bonding. It has been shown that various functional groups such as silanes, phosphonates, carboxylates, catechols, and amines are good candidates for covalent bonding with oxide covered inorganic substrates. Some examples of covalent bonding between functional groups of substrate and coating is shown in Figure 1.2.
As known from classical chemistry, generally covalent bonding is stronger than ionic bonding, therefore for better corrosion protection properties, covalent bonding between substrate and a coating material is highly desired. In general, there are two approaches to achieve the covalent bonding at metal/oxide/polymer interface. One is the modification of the surface with self-assembled monolayer (SAM) and then application of the coating material. The second approach is to coat the oxide surface with end functionalized polymers which leads to covalent bonding with the substrate. Both approaches have their own advantages and disadvantages, such as monolayers provide more molecular control, however, mechanical robustness is compromised. On the other hand, prefunctionalized polymer coatings has better barrier properties but the degree of covalent bonding between the substrate and a coating material is reduced due to steric hindrances.
1.3 Deadhesion of polymer coatings from metallic substrates

A complete polymer coating based protective system should provide an efficient barrier against water, oxygen and ionic species leading to life long protection of metallic substrate against corrosion. However, due to presence of defects, pores and cracks in an polymer coating system, water, oxygen and ions can approach metal/polymer interface. These corrosive species leads to corrosion of metal underneath the organic film by several mechanisms. Two possibilities which are of high technical importance are cathodic and anodic reactions at polymer/metal interface. In a corrosion reaction, both cathodic and anodic reactions occur at the same time, however, one of them will be the rate determining step. The metal ions produced due to anodic process, leads to increase in ionic force underneath the coating, giving rise to formation of blister due to osmotic phenomenon\textsuperscript{14}[pp. 510-515]. These blisters can grow by different mechanisms, known as, cathodic and anodic delamination.

1.3.1 Cathodic delamination

As mentioned in section 1.3, one mechanism of polymer coating deadhesion from the metallic substrate is cathodic delamination. It has been shown that the major driving force for cathodic delamination in presence of humid air is cathodic reaction (see equation 1.3)\textsuperscript{31}. The hydroxyl and metal ions produced as a result of cathodic and anodic reactions, respectively, can form complexes (specially for zinc and iron) and precipitate as metal oxides and hydroxides. Studies has also indicated that the pH beneath the coating, where cathodic reaction takes place is relatively high due to oxygen reduction reaction which produces hydroxyl ions\textsuperscript{32}. These very high local pH value leads to deadhesion at polymer/metal interface possibly due to breakage of covalent bonding between the polymer and the metal. The complete mechanism of cathodic delamination was proposed by Leidheiser et. al\textsuperscript{31} and can be summarized as follows.

- Corrosive species such as water, oxygen and ions penetrates through the polymer coating.
- Low resistance pathways are created between bulk electrolyte and the substrate.
- Anodic reaction leads to oxidation of metal at the surface.
- To compensate anodic reaction, corresponding reduction of oxygen (cathodic reaction) takes place at the metal surface and leads to initiation of delamination.
- Due to corrosion reactions in a confined area, corrosion products precipitates on the metal surface. This leads to drop in a pH at the anodic reaction site.
1.3. Deadhesion of polymer coatings from metallic substrates

- This causes the cathodic regions to be more basic (pH >10) and anodic regions more acidic (pH <10).

![Schematic representation of cathodic delamination of polymer coated zinc substrate.](image)

The effect of higher pH on the degradation of interfacial bond has been supported by the existence of carboxylated species at the interface\(^{33}\). On the other hand, at the anodic side of corrosion reaction, local pH value is relatively low (i.e. <10). The rate of cathodic delamination is determined by rate of diffusion of oxygen through the polymer coating (in the case where oxygen reduction reaction is dominant) and by diffusion of alkali metal cations through the coating to cathodic region\(^{32}\). It was also shown that the rate of cathodic delamination strongly depends on the coating thickness suggesting that the rate of diffusion of reactants through the coating was an important variable.

### 1.3.2 Anodic delamination

Cathodic delamination usually requires presence of ions, water molecules, and an electron conducting interface that allows electrochemical reactions to occur. Hence, cathodic delamination usually dominates at relatively high humidity levels and on materials which form (semi)conducting oxides. Whereas, for wet conditions with low humidity levels and insulating interfaces, such as aluminum, anodic-driven deadhesion reaction will be dominant\(^{34}\). Anodic deadhesion processes can be classified as chemical reaction that takes place underneath an organic coating in which the major deadhesion process is the anodic corrosion reaction\(^{15}\)[pp. 131]. This type of corrosion process is also termed as filiform corrosion (FFC) due to growth of thread like filaments\(^{35}\). Although FFC is more common on organic-coated aluminum\(^{36,37}\), it has been also observed on magnesium and steels\(^{36,38}\). It usually arises from surface defects present in the protective film in the presence of soluble ionic species. The mechanism of FFC is still debated. Various processes including cathodic disbondment\(^{39,40}\), anodic undermining\(^{41}\), and physical disbonding\(^{29,42}\)
though electro(osmotic) forces are proposed as the primary cause. As an example, consider FFC on organic coated iron, that consist of electrolyte filled filament heads, containing $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ cations and complexing anions. Generally, it is believed that under these conditions, the iron substrate is oxidized at the head front (anode) (see equation 1.9) and oxygen is reduced in the vicinity of the head-tail junction (cathode) (see equation 1.8). This leads to differential aeration because oxygen and water is supplied to the filament head by diffusion through the porous tail. The potential gradient created between anode and cathode, forces anions to migrate to the front and cations to the back. Oxidation of iron is thought to result in the undercutting of the organic coating at the filament head leading edge, and has been proposed as the principal cause of coating deadhesion.

\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- \\
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^-
\end{align*}

(1.7) (1.8)

### 1.3.3 Migration of species through polymer coatings

The life time of organic-coated systems strongly relies on the protective properties of a coating material. Polymer coatings not only reduce the rate of corrosion on metal but they also act as a barrier to the penetration of external species. Corrosion reactions underneath the polymer coating requires an aqueous medium (that provides conductivity) and species for the cathodic reaction (usually oxygen). As the corrosion process cannot proceed more rapidly than the slowest mechanistic step, limiting the rate of transport of one of the reactants will slow down the overall corrosion process. Hence, the transport of aggressive species (such as water and oxygen) through the polymer coating is a matter of concern and is discussed in the following subsection.

**Transport of oxygen**

The main cathodic reaction in the corrosion process at neutral pH is oxygen reduction (see figure 1.3). Hence, the diffusion of oxygen through the polymer coating plays a significant role in initiation and progression of a corrosion reaction. However, the effect of oxygen permeation through an organic coating is still debatable. For instance, Baumann has determined the oxygen permeability through several paint films and concluded that oxygen diffusion through a coating plays a role in defining the final rate of corrosion. While on the other hand, Mayne has stated that oxygen diffusion could not be a rate determining factor in the corrosion process. Moreover, Stratmann and coworkers have studied the effect of oxygen partial pressures on the delamination rate of epoxy based polymer coated iron substrate and estimated the diffusivity of molecular oxygen as $1.7 \times 10^{-8}\text{cm}^2\text{s}^{-1}$. The diffusion of oxygen through polymer coating strongly depends on the composition and morphology of the polymeric material. Specially, polymer films with less defects
and pores in a molecular structure could significantly reduce the diffusion of oxygen through the polymer matrix.

**Transport of water**

Water is one of the important partner in initiating a corrosion process underneath a polymer coating\textsuperscript{48}. The important question to know is how and at what rate the water approaches a polymer/metal interface. Does water permeate through the polymer matrix due to defects present in a coating or it just follow a random walk through the coating to approach an interface. Some of the previous studies have shown that the polymer glass transition temperature (\(T_g\)) strongly influences the solubility of water in a coating. In particular, low \(T_g\) leads to higher permeability of water through a coating which leads to higher corrosion rates\textsuperscript{49}. Moreover, permeation of water leads to swelling of a polymer film that induces internal stresses and as a result of these internal stresses the \(T_g\) of a coating can be lowered\textsuperscript{50}.

It has been demonstrated that water uptake of a polymer coating increases on applying cathodic potential\textsuperscript{51}. The increased rate of water uptake was a direct consequence of the development of more effective diffusion pathways through the coating. Hence, it is of technical interest to improve the barrier property of coatings against water permeation through the polymer. This can be achieved by increasing the coating thickness, low porosity, or by use of several layers of coating with additional additives (like pigments)\textsuperscript{14}[pp. 506-507]. The water uptake by organic films (applied or free standing) can be measured by weight measurements\textsuperscript{52,53} either as a weight gain during absorption or weight loss during drying. More practical and easier way to measure water uptake by organic films is by in situ capacitance determination using electrochemical impedance. Higher water content in a coating leads to higher capacitance values. Equation that is widely used to determine the water content in a organic film is Brasher-Kingsbury equation\textsuperscript{54}.

\[
\phi = \frac{\log[C_c(t)/C_c(0)]}{\log(80)}
\]  

where, \(\phi\) is the volume fraction of water in a coating. \(C_c(t)\) and \(C_c(0)\) are the coating capacitance at time \(t\) and of the dry coating, respectively.

**Transport of ions**

Organic coatings applied to metal surfaces in absence of inhibitive pigments retards the corrosion reaction by providing a barrier to the flow of ions\textsuperscript{46}. Studies have been made to reveal the factors which control this resistance and the mechanism by which ions flow through the polymer film. For instance, Kittleberger and Elm\textsuperscript{55} measured diffusion rate of sodium chloride through several layers of organic coating and found a linear relationship between the rate of diffusion and the reciprocal of the film resistance. This linear relationship suggests that sodium chloride diffused
through the coating as ions and not as ion pairs or undissociated molecules, since the diffusion through the unionized coating material would not affect the resistance. Furthermore, they also found that rate of diffusion of ions is much smaller than the rate of diffusion of either water or oxygen. To further verify this behavior, Mayne and coworkers\textsuperscript{56,57} conducted a study over cast varnish coating to determine the resistance of the film that is in contact with potassium chloride. They observed two opposite behaviors, either the conductivity increased with increasing electrolyte concentration or the conductivity decreased when the solution became more conductive. The interpretation of decrease in conductivity with reduced solution resistance was associated with water uptake by the film. Moreover, it was also concluded that increase in conductivity with increased electrolyte concentration was a result of differences in cross-linking density within the film structure.

1.4 Corrosion products

The corrosion products discussed in this section are the solid products formed at the surface of a corroding metal. Corrosion products formed are the first layers which are exposed directly to the environment, hence they greatly influence the corrosion behavior of the metal. Consequently, it is important to understand the process of corrosion product formation and what are the factors which effect them. In this section, the focus would be on the corrosion products formed as a result of zinc corrosion in aqueous solutions and how they can be used to fabricate nanostructures which can play a vital role in various application areas such as nanoelectronics\textsuperscript{58,59}, sensors\textsuperscript{60} and photocatalysis\textsuperscript{61,62}. Generally speaking, corrosion products differ in composition, structure, morphology, size, and properties depending on the conditions of the corrosion process\textsuperscript{63}[pp. 157].

1.4.1 Corrosion products of zinc in aqueous solutions

The most common corrosion product of zinc in diluted salt solutions such as KCl or NaCl at room temperature is ZnO, with zinc hydroxide present in various amounts as minor component\textsuperscript{63}[pp. 171]. Generally, ZnO is expected to crystallize by the dehydration of zinc complexes (such as zinc hydroxide) that are formed during zinc corrosion in aqueous salt solution\textsuperscript{64}. Moreover, in solutions of certain salts such as H$_3$PO$_4$, zinc can form compounds of low solubility (such as Zn$_2$P$_2$O$_7$) and corrosion products can be concentrated with the corresponding zinc compounds\textsuperscript{63}[pp. 171].

Effect of solution pH

The decisive factor in the formation of zinc corrosion product is the solution and surface pH. This dependency is illustrated in a Pourbiox diagram (1.4). This diagram describes the relative formation of species in a certain pH-potential region. For
instance, in acidic solutions, zinc has high solubility and dissolves with the formation of Zn\(^{2+}\) ions. However, no corrosion product could be formed on corroding zinc surface as zinc complexes are soluble under acidic conditions (pH <5)\(^{65-67}\). Solubility of zinc decreases as the solution pH increases, that results in the precipitation of Zn(OH)\(_2\) when certain pH value is approached. Roetheli et al.\(^{68}\) have studied the corrosion of zinc in HCl and NaOH aqueous solutions of different pH and has concluded that no corrosion product could be formed on the zinc surface when the solution pH was either below 5 or more than 13.5. The corrosion products formed on galvanized steel in various concentrations of alkaline solution (KOH) was studied by Macias and Andrade\(^{69}\). They found that initially the main corrosion product formed was ZnO, but it transforms to Zn(OH)\(_2\) for more than 30 days of immersion in a solution.

![Potential-pH equilibrium diagram (Pourbaix) for zinc.](image)

The morphology and structure of corrosion products formed in phosphate solutions also depends greatly on the solution pH\(^{71-73}\). The zinc phosphonate films formed are stable in the pH range of 3-12\(^{74,75}\). It was found that the film dissolved completely at low pH, whereas at high pH they are converted to Zn(OH)\(_2\), which then decomposes to ZnO or dissolves as zincate ions.

**Growth process**

One of the fundamental studies on the growth and transformation of zinc corrosion products in aqueous solutions has been conducted by Feitknecht\(^{76}\). It was found that amorphous hydroxide is precipitated from dilute solution of zinc chloride, and
changes with time to ZnO or Zn(OH)$_2$ via following reactions:

\[
\begin{align*}
Zn^{2+} + 2 OH^- & \rightarrow Zn(OH)_2 \quad (1.10) \\
Zn(OH)_2 & \rightarrow ZnO + H_2O \quad (pH = 7 - 9) \quad (1.11) \\
Zn(OH)_2 & \rightarrow \beta - Zn(OH)_2 \quad (pH = 11 - 12) \quad (1.12)
\end{align*}
\]

At higher Cl$^-$ concentration and more acidic pH values (pH<7), then two different hydroxide chlorides (a and b) can be formed by the following reaction mechanism.

\[
\begin{align*}
Zn(OH)_2 + Zn^{2+} + 2 Cl^- & \rightarrow 6 Zn(OH)_2 \cdot ZnCl_2 \quad (a) \quad (1.13) \\
7 Zn^{2+} + 12 OH^- + 2 Cl^- & \rightarrow 6 Zn(OH)_2 \cdot ZnCl_2 \quad (a) \quad (1.14) \\
4 ZnO + 4 H_2O + Zn^{2+} + 2 Cl^- & \rightarrow 4 Zn(OH)_2 \cdot ZnCl_2 \quad (b) \quad (1.15) \\
5 Zn^{2+} + 8 OH^- + 2 Cl^- & \rightarrow 4 Zn(OH)_2 \cdot ZnCl_2 \quad (b) \quad (1.16)
\end{align*}
\]

Similarly, zinc carbonates such as smithsonite (ZnCO$_3$) and hydroxycarbonate mixed salt hydrozincite [Zn$_5$(CO$_3$)$_2$(OH)$_6$] can be obtained by precipitating a solution of zinc salt with a mixture of sodium hydroxide and sodium carbonate. The composition of the corrosion product formed on zinc surfaces from different aqueous solutions may not be uniform and it has been shown by several research groups that formed corrosion layer varies depending on the corroding environment. The important properties of the corrosion product formed are compactness of the formed layer, adhesion to the substrate, electrical conductivity, hardness and resistance to dissolution. These properties determine the chemical stability and electrochemical properties of the formed zinc corrosion products.

1.4.2 Corrosion process for fabrication of Zn(O) nanostructures

Generally speaking, corrosion process is a highly undesired process which leads to a loss of material and product properties. However, in recent years it has been shown that corrosion process can be utilized to synthesize various nanostructured materials. In particular, by customizing the corrosion process, one could synthesize various nanostructured materials such as TiO$_2$, CdO, and CuO. As mentioned in section 1.4.1, corrosion is strongly influenced by oxygen content, solution pH, ion concentration, and surrounding environment, therefore to control and optimize the corrosion process, it is important to control these parameters. By using controlled corrosion process, several ZnO nanostructures has been synthesized. For instance, Yu et al. has fabricated ZnO nanorods on zinc foil by corrosion in aqueous formamide solution. The growth was initiated by immersing zinc foil in a 5 wt % formamide aqueous solution and heating at 65 °C for 24 h. The oxidation of zinc in water is relatively low due to presence of surface passivating layer. Therefore, formamide and high temperature was utilized to increase the release of zinc ions due to corrosion, which eventually leads to growth of uniform hexagonal ZnO nanorods that were highly oriented with the growth direction along the c-axis (perpendicular to the
substrate surface) by dehydration of zinc hydroxide complex. Using similar growth strategy, Zhang and coworkers\textsuperscript{87,88} have synthesized highly oriented and densely packed ZnO nanorods on zinc substrate by corrosion of zinc in formamide solution at 65 °C. The corrosion of zinc has been further utilized by Zhao and coworkers\textsuperscript{89} to synthesize pine nano-tree like structures on zinc foil. The synthesis of tree like structure was carried out by corrosion of zinc that was dipped in a aqueous solution of ethylenediamine and heating at 140 °C for 10 h. The resulting corrosion product was dense arrays of the complex nanostructures which resemble a 'pine-tree forest'\textsuperscript{89}. More recently, the substrate free fabrication of ZnO nanorod film was grown by hydrothermal approach\textsuperscript{90}, which again works on a principle of zinc corrosion and precipitation to form corrosion products. The overall growth mechanism of ZnO nanorods via hydrothermal approach is well documented\textsuperscript{91}, which is expressed by a following reaction.

\[
\text{Zn}^{2+} + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}
\] (1.17)

In hydrothermal approach, the rate of release of OH\(^-\) ions is controlled by addition of inhibitors such as hexamethylenetetramine (HMTA) which leads to the controlled crystallization of ZnO\textsuperscript{92}. The mechanism suggested by Wang et al.\textsuperscript{90} for substrate free growth of self supporting ZnO nanowire arrays can be expressed as follows.

\[
\text{Zn}^{2+} + n\text{NH}_3 \rightarrow \text{Zn(NH}_3)_n^{2+} \quad (n = 1, 2, 3 \text{ or } 4)
\] (1.18)

\[
\text{Zn(NH}_3)_4^{2+} + 2 \text{OH}^- \rightarrow \text{ZnO} + 4 \text{NH}_3 + \text{H}_2\text{O}
\] (1.19)

Examples from the literature shown above demonstrates the potential of metallic corrosion for the fabrication of ZnO nanostructures. Besides the good scalability, metal corrosion offers a economical way to prepare nanomaterials with greatly reduced energy consumption.
Chapter 2: Aims and Concepts

2.1 Motivation and aims of the work

Organic coatings are an important constituent of modern corrosion protection systems\(^9\). In particular, synthetic polymer coatings are widely applied to increase the durability of the protection system. For effective protection against corrosion, polymer coatings should have sufficient barrier properties and adhesion to the metal surface in presence of water, ions, and other corrosive species. The barrier properties of polymer coatings has been significantly modified by addition of additives and use of multi-lamellar coatings, which leads to reduced defects and pores in the coating\(^14\). Moreover, adhesion between metal and polymer has been enhanced by replacing physical adhesion forces to covalent bonding\(^94,95\). Current industrial protective polymer coatings are usually several micrometers up to tens of micrometers thick. From the application side, thinner coatings are desirable due to economic reasons, though it is hard to realize that the thinner coatings would have same barrier properties.

Deadhesion of polymer coatings from the metal or oxide substrate due to corrosive electrochemical processes is a common problem which could lead to complete loss of desired material properties. Particularly on steel, including galvanized steel, as well as on zinc, cathodic delamination starting on a electrolyte-filled defect is one of the main mechanisms of deadhesion of a coating\(^96,97\). However, the deadhesion process at polymer/metal interface is a more difficult problem due to lack of detailed understanding of bonding chemistry at polymer/metal interface. One of the problem behind this issue is that direct analytic probing of such a buried interface is difficult, as most available non-destructive experimental techniques are not interface-specific with the notable exception of sum-frequency generation spectroscopy\(^98,99\). Consequently, typically the interface is destroyed, and subsequently the detailed analytical features of surface analysis are available\(^13,94,100\). Therefore, it is crucial to develop coating methods and strategies that can lead to the better understanding of adhesion and deadhesion processes at metal/polymer interface. Ultrathin plasma polymer coatings have been considered as a possible alternate, however, poor understanding of interfacial bonding chemistry at polymer/metal interface still causes a problem\(^101\). As a pure analytic approach to an understanding of metal(oxide)/polymer interfaces can give only limited answers, here a synthetic approach is employed, in which the metal(oxide)/polymer interface is defined by
chemical synthesis. This synthetic approach permits to carry out detailed electrochemical experiments with the coating in place.

Thus, the primary aim of this work is to synthesize ultrathin polymer coatings that are covalently bound to a metallic surface and has a well defined interfacial chemistry. This approach allows the better understanding of interfacial chemistry at the metal/polymer interface and allows to systematically study the bonding and deadhesion behavior between polymer and a metal surface. In addition to the adhe-

Figure 2.1: Schematic representing the route for the delamination studies on modified zinc substrate. (a) Chemisorbed polymer coatings, (b) on ZnO nanostructured surface.

sion strength, oxide chemistry at the polymer/metal interface also plays a significant role in defining the final corrosion behavior. Most reactive metal substrates are covered with the native oxide layer, while during the corrosion process an oxide layer is formed as a corrosion product. Corrosion products formed on the metal surface could strongly influence the further corrosion of a metal. In particular, formed corrosion products can be passivating, that is blocking anodic and/or cathodic reactions, thus significantly reducing the rate of corrosion, or non passivating (having little or
no effect on the corrosion). The growth of these products depends on the corrosion environment and conditions such as pH, temperature, and humidity. Moreover, tailoring the corrosion process can lead to the fabrication of oxide nanostructures that are potential candidates for various optoelectronic applications. Hence, the other area of interest in this work is to study the corrosion products formed on the metal surfaces and how these products could influence the cathodic delamination process of organic coatings. Study of the corrosion products formed as a result of corrosion reaction could provide better understanding of the corrosion reactions taking place at the surface.

2.2 Approach

2.2.1 Surface of interest

Zinc is a widely used material for corrosion protection of steels. Moreover, it is often coated with polymers to enhance the corrosion protection properties. Therefore, in this work zinc is used as model substrate to study the deadhesion process at the polymer/metal interface. This allows to mimic the corrosion processes that takes place on galvanized steels that are coated with polymers.

2.2.2 Synthesis of chemisorbed polymer coatings

As mentioned earlier, the protective properties of organic coatings applied on metal surfaces are determined substantially by barrier properties of a protective coating and the adhesion strength between polymer and metal. Therefore, in order to enhance the adhesion strength, covalently bonded polymer coatings were synthesized in situ on top of metal substrates. Covalently bound polymer coatings on inorganic substrates are typically synthesized by two routes (a) a grafting to approach, where pre-synthesized end functionalized polymers are covalently bonded to the substrate or (b) by grafting from/onto approach where polymer is grown in situ on the solid substrate. A special case are ultrathin, highly cross-linked plasma polymer films. In this work, grafting onto approach to synthesize ultrathin covalently bound polymer coatings have been carried out. Initially, the zinc substrate was functionalized with small molecules having specific functional groups that leads to formation of covalent bonding between metal and an organic molecule. The advantage which small organic molecules have over end functionalized bulk polymers is that due to steric hindrance in end functionalized polymers, the number of covalent bonds between polymer and metal is significantly reduced. Hence, the deadhesion process can be accelerated due to less number of covalent bonds between metal and polymer.

The adhesion strength between metal and polymer is determined by the functional groups that are present in polymer which makes covalent bonding with the
In particular, polymer coatings with silane and carboxylic functionalities are often used in industrial polymer coatings because of their desirable structural and interfacial performances. Hence, organic molecules with functionalities that lead to silane and ester bonding were employed. The small chain length of the functionalizing molecule leads to a high degree of covalent bonding with well-defined interfacial chemistry. Later on, aliphatic (polymethylmethacrylate, PMMA) and aromatic (Polystyrene, PS) polymers were grown on top of the functionalized zinc substrate by performing thermally initiated free radical polymerization using the vinyl functionality as polymerizable group in the anchoring molecule. This synthesis strategy leads to ultrathin linear polymer coatings with well-defined interfacial chemistry that can be used to fundamentally study the deadhesion behavior and bonding strength at polymer/metal interface.

The other factor which also plays a vital role in protection of metal against corrosion is permeability of aggressive species such as water and oxygen through the polymer coating. Water and oxygen can access metal surface due to presence of pore and defects in a polymer bulk structure. The diffusion of these aggressive species through the polymer coating can be significantly reduced by increasing the degree of cross-linking between the polymer chains. Therefore, in addition to linear coatings, cross-linked polymer coatings with varying degree of cross-linking were also synthesized. The polymer chains were cross-linked by addition of bi-functional vinyl...
molecule during the polymerization reaction. The different amount of cross-linker leads to polymer coatings with varying degree of cross-linking that exhibits different degree of permeation level for water and oxygen.

\[
\text{Silane}
\]

Figure 2.3: Schematic representation of synthesis of PMMA and PS polymers (linear and cross-linked) on silane functionalized zinc.

2.2.3 Model corrosion experiments

Scanning Kelvin probe (SKP) is a well established technique to study the deadhesion of polymer coatings from metal substrates due to cathodic delamination\textsuperscript{118,119}. Hence, SKP was used as a primary analytical technique to study the deadhesion behavior at polymer/metal interface. Moreover, linear polarization experiments were performed on these chemisorbed polymer coatings to study the effect on corrosion behavior of zinc.
2.2.4 Study of corrosion products

Corrosion products that are formed during the corrosion reaction can substantially influence the further corrosion process taking place on top of coated metal surfaces\cite{120,121}. Hence, it is of interest to study the corrosion products that are formed during the corrosion process. In this work, the corrosion process was monitored by performing in situ Raman experiments during the cathodic delamination process. This allows to study the chemical and crystal structure of oxide formed as a corrosion product during the cathodic delamination process.

2.3 Thesis outline

Figure 2.4 schematically represents the outline of the thesis. Apart from the first three chapters, present work can be divided in to three parts A, B and C.

First part (A) corresponds to Chapters 4, 5, 6 and 7 in which the delamination kinetics of ultrathin chemisorbed PMMA and PS coatings has been discussed. Chapter 4 investigates the delamination kinetics of silane bonded PMMA coating to a zinc substrate. The corrosion properties has been studied using SKP, linear polarization experiments, and EIS. Chapter 5 represents the studies on the cathodic delamination kinetics of silane bonded PS coatings using SKP, while Chapter 6 investigates the delamination kinetics of ester bonded PMMA coating. The overall comparison of differently bonded PMMA and PS coatings has been discussed in Chapter 7.

Second part (B) of this thesis corresponds to Chapter 8, which investigates the effect of different ZnO morphologies grown on zinc substrate on the cathodic delamination. Different ZnO structures namely twin-plate, nanorod and sphere were grown on top of zinc via a hydrothermal approach and their delamination kinetics has been studied using SKP.

Third part (C) of this thesis corresponds to Chapters 9 and 10. This part shows the investigation of growth of ZnO nanorods on zinc substrate via a tailored corrosion process at room temperature. The growth mechanism of ZnO nanorods has been discussed in Chapter 9, while the growth kinetics of ZnO nanorods studied via in situ Raman spectroscopy is discussed in Chapter 10. Each chapter also consists of the introduction part, where the topic is specifically introduced.
2.3. Thesis outline

Figure 2.4: Layout of flow chart depicting the schematic of thesis chapters.
Chapter 3: Experimental Techniques

The aim of this section is to give a brief introduction to the experimental techniques employed for the analysis of the samples as well as to provide the details about how the samples were prepared and characterized.

3.1 Analytical techniques for characterization of surface modification

3.1.1 Infrared (IR) spectroscopy

IR spectroscopy is a well established technique for identification and characterization of the molecular structure, orientation and intermolecular bonding of organic molecules adsorbed on metallic and non metallic surfaces. Vibrational spectra are used as characteristic fingerprints for adsorbate molecule, adsorption configuration and structures. If a molecule has a dipole moment, then a molecule can absorb the IR light, however, only at certain fixed frequencies. Thus, an IR spectrum of light reflected from surface will show absorption peaks that are characteristic of molecule and its mode of bonding to the surface. These are the basis of IR spectroscopy. FTIR spectroscopy is nothing but just the Fourier transform of the reflected light from the molecule that is under investigation\textsuperscript{122}.

In this work, modified samples were characterized by IR measurements performed on a Bruker Vertex 70v Fourier transform IR spectrometer (Bruker, Karlsruhe, Germany). IR spectra were taken with a spectral resolution of 4 cm\textsuperscript{-1} at an angle of incidence of 80° using p-polarized light. A liquid nitrogen cooled, middle band mercury cadmium telluride detector was used for detection. Prior to surface modification, background spectra were obtained from freshly cleaned zinc samples. The reflectance absorbance spectra shown in this work were recorded against these backgrounds.

3.1.2 X-ray photoelectron spectroscopy (XPS)

XPS is a powerful surface sensitive technique that is widely used for the surface analysis of materials. XPS works on the principle of photoelectric effect that is used for obtaining qualitative and quantitative information about the elemental
composition and of the surface. When the sample surface is bombarded with X-rays having characteristic energy, the electrons from the core levels of the sample are emitted. The energy of these emitted electrons is a “fingerprint” of the each element present in a material and their chemical environment. Consequently, XPS provides elemental specificity and the chemical environment of the elements present at the surface.

To analyze the surface composition, modified zinc samples were characterized using XPS (Quantum 2000, Physical Electronics, Chanhassen, MN, USA) at a take-off angle of 45°, with a monochromatic Al Kα source (1486.6 eV) at a pass energy of 23.5 and energy resolution of 0.2 eV. Survey scans were performed to scan the sample for relevant elements (pass energy = 100 eV, energy step = 0.5 eV). Measurements were formed by Adnan Sarfraz.

3.1.3 Time-of-Flight secondary ion mass spectrometry (TOF-SIMS)

TOF-SIMS is also a well developed surface sensitive analytical technique that uses a pulsed ion beam to remove molecules from the very outermost surface of the sample. The molecules become dissociated ions (positive or negative) after the bombardment with the incident ion beam. These generated secondary particles are then accelerated into a flight path on their way towards a detector and their mass is determined by measuring the exact time at which they reach the detector (i.e. time-of-flight). The 'Time-of-Flight' of an ion is proportional to the square root of its mass, thus all the different masses are separated during the flight and can be detected individually.

In this work, TOF-SIMS was used as a tool to analyze the interfacial region at metal/polymer interface. TOF-SIMS measurements have been executed with a PHI TRIFT CE (Physical Electronics), applying a gallium ion gun on a spot size of 100 µm × 100 µm. The primary gallium ion beam was used with an energy of 15 kV and the same ion beam was used for sputtering on a spot size of 200 µm × 200 µm to remove ambient impurities before measuring the mass spectrum. Experiments were conducted by Adnan Sarfraz.

3.1.4 UV/Vis spectroscopy

UV/Vis spectroscopy is a widely used technique to study the optical properties of materials. It uses light in ultraviolet-visible range to induce electronic transitions in a molecule/material under investigation. It is well known that when a material is irradiated with a light, it absorbs some light having a wavelength that matches a possible electronic transition within the molecule and excites an electron from ground state (HUMO) to an excited state (LUMO). By studying the reflectance/absorption spectra of the exposed sample, one could draw useful information about the concentration of the molecule or the optical properties of a material.

In this work, UV/Vis spectroscopy was employed for two primary experiments.
3.2. Analytical techniques for characterization of corrosion behavior

One was to study the degradation of a dye (MO) under the visible light illumination and in presence of a catalyst. Second was to study the optical properties of as synthesized ZnO nanostructures. The UV/Vis spectrometer used in this study was Perkin Elmer Lambda 900.

3.1.5 Ellipsometry

Ellipsometry is an optical technique that is widely used to determine the thickness and optical constants of thin films. It is based on the measurement of change in the polarization of light after reflection at normal/non-normal incidence on the surface to study. Usually in ellipsometry linearly polarized light is used which becomes elliptically polarized after reflection from the surface of interest or vice-versa. Ellipsometric measurement gives two independent angles i.e. $\Delta$ and $\Psi$, where $\Psi$ is the amplitude ratio and $\Delta$ is the phase difference of p and s-polarized light. Ellipsometry is an absolute measurement method i.e. it does not need any reference. However, it does not give directly the physical parameters of the sample (thickness and refractive index). In order to describe the sample it is always necessary to use the model\textsuperscript{126}.

To determine the thickness of as synthesized polymer coatings, ellipsometric measurements were performed using a UV/visible spectroscopic ellipsometer (SE 800, Sentech Instruments GmbH, Berlin/Krailling, Germany) in the wavelength range of 400-800 nm. Measurements at three spots per sample were taken with an incident angle of 70°. Differences in ellipsometric parameters with respect to the bare zinc substrate were analyzed. Film thickness of the polymer layer on samples, regardless of modification, was obtained by fixing the refractive index of the polymer coatings to 1.5, and considering it in first approximation as wavelength-independent. The value of 1.5 is close to the refractive index of PMMA of $\approx 1.48$\textsuperscript{127}.

3.2 Analytical techniques for characterization of corrosion behavior

3.2.1 Scanning Kelvin probe (SKP)

SKP is a well established technique to study the deadhesion behavior of polymer coatings from metal/semiconductor surfaces. In principle, SKP measures a Volta potential (or work function) distribution over metal or semiconductor surfaces using a vibrating capacitor method\textsuperscript{47,128,129}. Kelvin probe usually consist of a conducting tip that is electrically in contact with the sample that is measured. When the work function of the tip and the sample is different, there will be a flow of current from one materiel to another in order to align the Fermi levels. The Volta potential difference is measured by zeroing the flow of the above mentioned current/electrons by applying external voltage. This applied external voltage, which is identical to the
Volta potential difference, is given by the energy difference between the Fermi level of the sample with respect to the Fermi level of the probe, which is known in many cases\textsuperscript{34}. The work function of a bare metal surface under high vacuum conditions is a well-defined quantity\textsuperscript{34}. However, when the metal surface is covered with an electrolyte or polymers, then electron has to pass through additional interfaces and the Volta potential differences is strongly affected by potential differences at these interfaces. The same applies to the electrode potential and hence, there is a simple relationship between Volta potential difference ($\Delta \Psi_{\text{Ref Pol}}$) and the electrode potential $E_{\text{corr}}$:

$$E_{\text{corr}} = \left\{ \frac{W_{\text{Ref}}}{F} - \chi_{\text{Pol}} - \epsilon_{1/2}^{\text{Ref}} \right\} + \Delta \Psi_{\text{Ref Pol}}$$  \hspace{1cm} (3.1)

$W_{\text{Ref}}$ corresponds to the work function of the reference metal, $\chi_{\text{pol}}$ is the potential of polymer surface and $\epsilon_{1/2}^{\text{Ref}}$ is the half-cell potential of the reference metal. Therefore, SKP allows the measurement of corrosion potentials without touching the surface under investigation across a dielectric medium of infinite resistance. For the reactive metals such as zinc, the surface is usually covered with a thin native oxide layer that significantly influences the reactivity at the composite. In such a case, the Volta potential difference is given by the sum of the potential differences over all interfaces\textsuperscript{34}. In case of cathodic delamination, an additional liquid interface is formed between metal/oxide and polymer. In such a case, metal/liquid interface is treated as conventional electrochemical interface, however, an additional galvanic potential difference $\Delta \Phi_D$ is taken into account for electrolyte/polymer interface.

$$E_{\text{corr}} = \frac{W_{\text{Ref}}}{F} - \chi_{\text{Pol}} - \epsilon_{1/2}^{\text{Ref}} + \Delta \Psi_{\text{Ref Pol}} + \Delta \Phi_D$$  \hspace{1cm} (3.2)

Therefore, ($\Delta \Psi_{\text{Ref Pol}}$) allows the measurement of corrosion potential at the metal/polymer buried interface only if $\Delta \Phi_D$ is known\textsuperscript{34}.

Delamination experiments were performed on a commercial SKP system from KM Soft Control (Wicinski - Wicinski GbR, Wuppertal, Germany) with a 100 $\mu$m NiCr tip in humid air and nitrogen atmospheres. Kelvin probe was calibrated to the standard hydrogen electrode (SHE) against a Cu/CuSO$_4$ reference electrode.

### 3.2.2 Linear polarization

Linear polarization is an electrochemical technique that estimates the rate of corrosion of metals by measuring the corrosion current. When a coated metal surface is exposed to a conducting electrolyte of sufficient oxidizing power, the metal will start to corrode by oxidation of metal referred as anodic reaction. The dissolution of metal leads to formation of free electrons which will flow to the cathodic side, where they will be consumed by a reduction reaction. However, direct measurement of corrosion current ($i_{\text{corr}}$) is difficult as anodic and cathodic sites shifts during the
3.2. Analytical techniques for characterization of corrosion behavior

corrosion. This problem can be resolved by applying external potential shifts (E),
which will produce a measurable current flow (I) at the corroding electrode. The
behavior of this externally imposed potential is governed by degree of difficulty in
anodic and cathodic reactions, which is termed as polarization resistance ($R_p$). The
smaller the rate of anodic and cathodic reaction, the smaller the value of $R_p$ for the
given potential shift. This current can be related to $i_{corr}$ by the following relation,

$$R_p = \frac{\beta_a \beta_c}{2.3 \ i_{corr} (\beta_a + \beta_c)} \quad (3.3)$$

where, $\beta_a$ and $\beta_c$ are Tafel slopes of anodic and cathodic branches, respectively.

In this work, linear polarization experiments were executed in 0.1 M KCl elec-
trolyte by using a Volta-lab Radiometer PST050 potentiostat at a scan rate of 5
mV/s. All experiments were performed in a self-made 3 electrode setup. As counter
electrode, a graphite stick was used. A commercial Ag/AgCl/3 M KCl reference
electrode (Metrohm, Filderstadt, Germany) served as reference electrode. All po-
tentials are quoted here versus standard hydrogen electrode (SHE). The corrosion
current densities $i_{corr}$ were calculated from the polarization resistance $R_p$ according
to an established procedure.$^{130}$ $R_p$ was determined as the slope of the linear polar-
ization curve from -15 mV to +15 mV around $E_{corr}$. The Tafel slopes of the anodic
and cathodic branch, $\beta_a$ and $\beta_c$, respectively, were obtained from linear regions of
the Tafel plots. Corrosion current densities were then calculated as.$^{130}$

3.2.3 Electrochemical impedance spectroscopy (EIS)

EIS is a useful analytical tool to study the properties and performance of polymer
coated metal systems. The AC impedance of an electrochemical cell is conventionally
measured by applying an AC potential and then measuring the current through
the cell. The ratio of potential and current is impedance of the cell, at a certain
frequency.$^{131}$

Using a Gamry PCI4/Series G Family potentiostat (Gamry Instruments Inc.)
with the same electrode setup as for linear polarization experiments, electrochemical
impedance spectroscopy (EIS) was performed in the frequency range of $10^{-1}$ to
$10^5$ Hz (10 points/decade of frequency $f$) with 15 mV amplitude of the sinusoidal
voltage modulation, at the corrosion potential. The experiments were conducted in a
borate buffer solution, containing 0.2 M $\text{H}_3\text{BO}_3$, 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ and 0.1 M $\text{Na}_2\text{SO}_4$.
The pH of the solution was measured as 8.4 ± 0.4. The used electrolyte provides
good conductivity to perform the EIS experiments, and is expected to suppress
undesired formation of (sometimes protective) corrosion products. Samples were
PVB coated, and have been prepared as for the SKP measurements. No strong
changes in the spectra have been observed after even several hours of exposure time
to the solution, as water uptake starts to be decisive only after >24 h. Echem
Analyst software (Gamry Instruments) has been used for fitting of the obtained
data.

3.3 Analytical techniques for characterization of corrosion products

3.3.1 Electron microscopy

Generally speaking, electron microscopy is primarily used to study the structure and morphology of a material that is not visible to our naked eyes or to a light microscope. It uses a beam of electrons to create an image of the specimen. Two major types of electron microscopes in use today are scanning electron (SEM) microscopy and transmission electron microscopy (TEM). In SEM, the image is created by secondary electrons that are emitted from the surface due to excitation by the primary electron beam. While in case of TEM, the image is created by a partially transmitted electron beam through a very thin specimen that carries information about the structure of the sample.\(^\text{132}\)

In this work, the surface morphology of the samples were obtained by using SEM from Zeiss (LEO 1550 VP) which was also equipped with energy dispersive X-ray spectrometer (Oxford Instruments). TEM measurements were performed by A. Kostka using JEOL JEM-2200FS operated at 200 kV.

3.3.2 Atomic force microscopy (AFM)

AFM is a tool that measures a topography as well as physical properties of a surface by scanning over the sample via a sharpened tip. The measurement principle of AFM is based upon the forces acting between the surface and a tip also known as cantilever. In order to measure the surface topography, the probe is placed close enough to the sample such that it can interact with the forces associated to the surface. The AFM tip scans across the sample surface by keeping forces between the sample and probe constant. The image of the surface is reconstructed by monitoring the precise motion of the tip which moves towards or away from the surface during the scan depending on the forces acting on it. In commercial AFM systems, multiple measurement modes are present such as contact mode and tapping mode. In contact mode, the tip is dragged across the sample surface and the surface topography is measured by looking at the deflection of the sample. In tapping mode, the cantilever is driven to oscillate near its resonance frequency close to the surface and the surface morphology is measured by detecting the changes in the oscillation of the cantilever.\(^\text{133}\)

In this work, AFM images were recorded by a Digital Instruments Dimension 3100 AFM in tapping mode, employing Si micro-cantilever tips with radius <10 nm and a resonant frequency of ~318 kHz. The measurements were performed by Asif Bashir.
3.3.3 X-ray diffraction (XRD)

XRD is a type of analytical technique that reveals the information about the crystal structure, chemical composition and physical properties of a material. In XRD the sample is illuminated with an X-ray (while either moving the sample or a detector), that leads to a diffraction pattern. These diffraction patterns are then analyzed to understand the crystallographic properties of a material. In order to analyze thin films, XRD is performed in a grazing incidence (GI) geometry. GIXRD employs low incident angles for the incoming X-ray beam, so that diffraction can be made surface sensitive\textsuperscript{134}.

In this work, XRD (Bruker-AXS D8) measurements were performed in a grazing incidence geometry with a Cu-K\textsubscript{\alpha} as a X-ray source.

3.3.4 Raman spectroscopy

Raman spectroscopy is a useful non-destructive analytical tool that is widely used to study the structure and properties of various types of organic and inorganic materials. Raman spectroscopy works on the principle of inelastic scattering of a monochromatic light that provides molecular fingerprint related to the vibrational, rotational, and other low frequency transitions of molecules\textsuperscript{135}.

In this work, Raman spectroscopy was employed to study the growth kinetics and properties of ZnO nanostructures. In situ measurements on the growth of ZnO nanowires were conducted using a Horiba Jobin Yvon LabRAM confocal Raman microscope with a Argon laser as a light source (emission wavelength; 514.342 nm) and a power of 12 mW. To carry out in situ Raman measurements, the assembly of sample mounted on zinc substrate was introduced into a custom made chamber with a glass window opening to allow spectral acquisition. To minimize electrolyte evaporation, the humidity was controlled \(\geq 90\%\) with the help of humid/dry air flow. Ex situ measurements were performed via alpha300M confocal Raman microscope system (Witec, Ulm, Germany), with an argon laser source (emission wavelength: 532 nm). For photoluminescence experiments, the UV laser source was employed with an emission wavelength of 355 nm. Measurements were performed through microscope objective of 100x (numerical aperture = 0.75) in reflection geometry.

3.4 Sample preparation

3.4.1 Materials

Zinc sheets (purity, 99.95\%) with a thickness of 1.5 mm were obtained from Goodfellow (Cambridge, UK). Vinyltrimethoxy silane (VTS), ethylene glycol diacrylate (EDA), hexanediol diacrylate (HDA), methyl methacrylate (MMA), styrene, azobisisobutyronitrile (AIBN), hexamethylenetetramine (HMT), toluene, and tetrahydrofuran (THF) were supplied by Sigma-Aldrich (Steinheim, Germany). MMA was
purified by distillation from CaH$_2$ under N$_2$ atmosphere, while AIBN was recrystallized in ethanol prior to use. All other chemicals were used as received unless otherwise noted. Zinc substrates (15 mm × 15 mm) were initially mechanically ground with SiC paper up to 4000 grit, followed by polishing with silicon paste (1 µm) to have a smooth surface. Polished samples were ultrasonically cleaned in acetone and dried under a nitrogen stream. Prior to functionalization, zinc substrates were immersed in 0.1 M NaOH for 1 min to increase the concentration of hydroxyl groups$^{12}$. The substrates were then thoroughly washed with deionized water. All synthesis steps were performed under air exclusion in standard Schlenk tubes.

### 3.4.2 Surface modification

**Functionalization of zinc with silane**

The overall scheme surface modification is illustrated in Figure 2.2. After the hydroxide treatment, zinc surfaces were modified with VTS by a silanization reaction$^{136}$, to obtain a vinyl-terminated, silane modified substrate. Functionalization was carried out at a room temperature by immersion of a polished zinc substrate in an ethanol/water mixture (90:10) containing 0.007 M of VTS. After 24 h, the sample was removed, cleaned sequentially with excess acetone and ethanol to remove physisorbed molecules, and dried under a pressurized nitrogen stream.

**Functionalization of zinc with ester**

The overall synthesis strategy is illustrated schematically in Figure 2.2. Functionalization reaction was carried out by adding 0.0275 mol of triethylamine in a 40 mL of anhydrous THF. The reaction mixture was then cooled down to 0 °C with a ice bath. Afterward, 0.0075 mol of acryloyl chloride was added drop wise under a continuous stirring over a period of 15 min. Zinc sample was then introduced in to a solution and reaction temperature was raised to room temperature by removing the ice bath. After 24 h, the sample was removed, cleaned sequentially with excess acetone and ethanol to remove physisorbed molecules, and dried under a pressurized nitrogen stream.

**Synthesis of polymer coatings**

For polymerization reactions, initially toluene (40 mL) was degassed by performing three freeze-thaw-pump cycles. Subsequently, MMA/styrene was added to reach a final concentration of 0.007 M, and AIBN was added to the solution in a concentration of 1 wt% relative to MMA/styrene. The mixture was stirred until a homogeneous solution was obtained. A functionalized zinc sample was then introduced into the reaction mixture and the temperature was raised to 70 °C in order to initiate a polymerization reaction. After 24 h the zinc sample was removed, washed
3.4. Sample preparation

with excess acetone, followed by ultrasonic cleaning for 1 min in a toluene solution in order to remove any remaining traces of polymer which is not covalently linked to the zinc. Later, the samples were dried in a nitrogen stream.

For the preparation of polymer coatings with different cross-linking densities on zinc substrate, the same polymerization procedure was employed, with different molar fractions (25% or 50%) of the respective cross-linking agent (EDA or HDA) added to the solution. The total monomer concentration (EDA/HDA + MMA/styrene) was kept constant.

3.4.3 Synthesis of ZnO nanostructures

Hydrothermal growth of ZnO nanostructures

A solution containing zinc nitrate hexahydrate \( \text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) and hexamethylenetetramine (HMT) was prepared in ultrapure water, containing each at a concentration of 50 mM. The solution was stirred at room temperature with a magnetic stirrer at 1200 rpm until a clear solution was obtained (10 min). For the synthesis of rod-like ZnO, the obtained solutions were directly heated (see below) without any capping agent. For the synthesis of twin-plate-shaped ZnO, gelatin was dissolved in the obtained solution with a concentration of \( 5 \text{ g.L}^{-1} \). For the synthesis of spherical ZnO particles, a 40 mM solution of trisodium citrate (\( \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \)) in ultra-pure water is mixed with the \( \text{Zn(NO}_3\text{)}_2/\text{HMT} \) solution with a volume ratio of 1:2 in a glass beaker.

Next, a clean polished Zn sheet substrate was put into the respective solution in a glass vial. The vial was tightly closed and then placed inside an oven for 90 min at a temperature of 90 °C. After letting the solution cool down to room temperature, the modified zinc substrates were removed from the solution and washed several times with water and then with ethanol to remove contaminants. Finally, the samples were dried in a nitrogen stream and kept in a desiccator until used.

Growth of ZnO nanorods via tailored corrosion route

Initially polished zinc sheets (1 cm × 1 cm × 1.5 mm) were spin coated with 5 weight% solution of PVB in ethanol, followed by drying, to obtain a \( \approx 2 \mu\text{m} \) thick polymer layer. Afterwards, the coated sample was placed on a zinc base plate and a reservoir was built at the edge of the sample for electrolyte insertion with the help of fast drying two component adhesive. Subsequently, a small defect was created at the edge of the coated sample with the help of a blade. The assembly was then placed into a self-made humidity chamber. In order to initiate the growth of ZnO nanorods via a tailored corrosion process, few drops of 0.1 M (unless noted otherwise) aqueous KCl solution was added. Finally, after 6-8 h the electrolyte was removed and substrates were washed with water and dried in an \( \text{N}_2 \) flow at room temperature.
3.4.4 Electrochemical evaluation of stability of polymer coatings

The electrochemical stability of coatings were carried out by using SKP, linear polarization and EIS (unless otherwise noted).

Prior to SKP experiments, zinc samples were spin coated with 5 wt% poly(vinyl butyral) [PVB] in ethanol to yield a ≈1 µm thick polymer film. This PVB coating prevents the spreading of the electrolyte above the modified zinc samples. Unmodified zinc substrates were spin coated with PVB and delamination experiments were performed under similar conditions to evaluate the effect of PVB alone. In order to initiate a cathodic delamination process, an artificial defect was created at the edge of the sample with a scalpel, and the defect was filled with 1 M KCl. The samples were subsequently introduced into a SKP chamber at 92% to 95% relative humidity and at a temperature around 23 °C. The progress of the delamination front was analyzed as described elsewhere\(^\text{12}\). As position of the delamination front, the first point which shows the potential of the intact interface was used. Typically, 3 to 5 samples for each given preparation were analyzed. The results presented are results of the median sample, i.e. after sorting the samples in the order of increasing stability, the sample with the middle performance was selected for presentation.

3.4.5 Photocatalytic decomposition of methyl orange (MO)

Photocatalysis experiments were performed in a home made continuous flow setup which is depicted schematically in Figure 3.1. Zinc foil with ZnO nanorods grown on top was placed on the bottom of a crystallization dish. Next to the foil, a magnetic stirrer was placed on the bottom of the dish. Initially, a \(10^{-5}\) M aqueous solution of methyl orange (20 mL) was added into the dish, and the solution was stirred with the help of a magnetic stirrer throughout the experiment.

![Figure 3.1: Schematic representation of in situ photocatalysis experiment.](image)

Before starting the photocatalytic decomposition of MO, ZnO nanorod arrays were immersed in to the reaction chamber for \(\sim 30\) min without illumination to
establish adsorption/desorption equilibrium. Part of the MO solution was then pumped into a quartz flow cell, placed inside a UV/visible spectrometer (Perkin Elmer Lambda 900), using a peristaltic pump at a flow rate of 50 µL s⁻¹. To ensure the presence of only a specific visible wavelength of light, the sample in the glass reservoir was illuminated with a HeNe laser (633 nm, 1.96 eV) of 20 mW power output with a beam expander, yielding a power density of ~10 mW cm⁻² at the location of the ZnO nanorods. The degradation of the dye was monitored using the UV/visible spectrometer by measuring the absorption spectra at different intervals, and evaluating the peak absorbance at 464 nm. The molar absorption coefficient of MO at 464 nm was determined as 4 · 10⁵ L·mol⁻¹·cm⁻¹ from a concentration series.
Chapter 4: Delamination kinetics of ultrathin PMMA model coatings on zinc bound via organosilanes

4.1 Introduction

Cathodic delamination studies have recently focused on the role of ion transport\textsuperscript{13,137}, including quantification of transport rates\textsuperscript{138}. Migration, rather than diffusion has been shown to be an important process for transport along the interface\textsuperscript{139}. The effect of surface morphology was also investigated\textsuperscript{19,140}. Comprehensive parameter scans have been carried out\textsuperscript{141}. For a better understanding of the chemical processes, delamination experiments have been combined with infrared spectroscopy\textsuperscript{142}. Mathematical models of the electrochemical processes have been developed, which permit a detailed analysis of the kinetics\textsuperscript{143}. Most studies leave the surface chemistry ill-defined, or use complex industrial coatings, which permit only a global understanding of the processes. Nevertheless, the detailed understanding of the electrochemistry has lead to novel coatings with self-healing properties\textsuperscript{8,144}.

Investigations of the direct linkage of coatings to the surface is subject of current interest\textsuperscript{94} and, e.g., bifunctional silane linkers have been found to decrease degradation rates\textsuperscript{95}. To overcome problems with the definition of interfacial chemical bonds, here an approach were an ultrathin polymer coating was synthesized is presented. Metallic zinc substrates were modified with vinyltrimethoxysilane (VTS), defining the covalent linkage at the metal(oxide)/polymer interface. Subsequently, these surface-functionalized zinc substrates were subjected to a thermally-initiated copolymerization of methyl methacrylate (MMA) in the presence or absence of crosslinkers. Resulting poly(methyl methacrylate) [PMMA] coatings have been characterized and their delamination behavior has been studied using SKP and electrochemical linear polarization experiments.

*This chapter contains results published as a scientific article:


35
4.2 Results and discussion

4.2.1 Surface modification

Zinc samples were first treated with a reactive silane coupling agent (VTS) that contains a polymerizable vinyl group. As shown in Figure 4.1, the zinc surface was modified with VTS via hydrolysis of the monomer in ethanol/water (90:10) mixture at room temperature. The addition of water to the reaction mixture promotes the hydrolysis of methoxy groups that are present in VTS, resulting in the formation of Zn-O-Si bonds, as will be shown below.

![Scheme of the surface modification steps carried out in this chapter.](image)

To examine the composition of the functionalized zinc surface IR, XP and mass spectra were recorded. Figure 4.2a shows an IR spectrum of a VTS-modified zinc surface. The bands at 3020, 2965, 2921, and 2850 cm$^{-1}$ are assigned to C–H stretching vibrations. Furthermore, the peaks at 1265, 1110, 1018, and 824 cm$^{-1}$ are modes typically observed for organic siloxane-based structures. The modification of the zinc surface with VTS was further verified by conducting XPS measurements. Figure 4.2b shows a high-resolution XP spectrum of the Si 2p signal at the functionalized zinc sample. The presence of this Si 2p signal can be clearly identified, indicating the presence of the silicon on the zinc surface.
Figure 4.2: (a) IR spectrum of VTS-modified zinc. (b) Si 2p region of the XP spectrum of VTS-modified zinc. The presence of the signal confirms the presence of silane on the surface.

To further verify the presence of chemical bonding between zinc and the silane coupling agent, ToF-SIMS analysis was performed. Initially, the top layer of VTS was sputtered away by ion etching, to analyze the interfacial region between the native oxide on zinc and the organosilane. In the region between organic film and native oxide, the fragment ZnOSi$^+$ was detected, as shown in Figure 4.3. The ion pattern of the fragment ZnOSi$^+$ should reflect the isotopic abundance of the elements present; the observed distribution is in close agreement to the calculated distribution$^{152}$. Deviations at the peaks of species with lower abundance at $\approx$109 amu and $\approx$111 amu are attributed to contributions of organic fragments to the totally measured count rate. The presence of the ZnOSi$^+$ fragment is an indication of the formation of a covalent bond between organosilane and the native oxide on zinc$^{152}$. It is known that hydrolyzed alkoxysilanes may react with each other to form a dense polymeric film on the surface$^{146}$, while care is needed to ensure the formation of a monolayer$^{136,153}$. Here, ellipsometric analysis yields a thickness of 2-3 nm of the silane layers, clearly above monolayer coverage, but still significantly below 10 nm.

Formation of a covalent bond between PMMA and the VTS-modified surface was achieved by performing a thermally initiated free radical polymerization of MMA in the presence of the modified zinc substrate with AIBN as initiator (see Figure 4.1). Two fractions of PMMA after the copolymerization reaction were obtained, a covalently surface-bound fraction and a fraction without covalent bond to the surface. The fraction that is physisorbed on the surface was washed with excess toluene to remove the nonbounded polymer. Figure 4.5 1a shows the measured IR spectra after copolymerization. Appearance of characteristic C=O stretching mode as a band at 1735-1740 cm$^{-1}$ is an indication of the presence of an acrylate bound to the zinc sample$^{150}$. In addition to copolymerization with the monofunctional monomer, polymerization was also carried out in the presence of bifunctional acrylates with different chain length and different molar fractions (25% and 50%).
Figure 4.3: SIMS showing the isotope distribution of ZnOSi\(^+\) fragments from the surface of VTS-modified zinc. Expected isotope distribution is shown as vertical lines (||) ca. 0.3 amu below the experimental peak.

Figure 4.4: XPS survey spectrum on chemisorbed PMMA coating without cross-linker. Absence of substrate peak indicates the uniform coverage of the surface.
The presence of such monomers in the copolymerization results in films consisting of cross-linked polymers. Figure 4.5 Ib-e shows the IR spectra of polymer films prepared in the presence of cross-linker. Furthermore, XP spectra (Figure 4.5 II) of polymer-modified samples show the expected C 1s and O 1s peaks. The high resolution C 1s spectrum can be decomposed into four distinct peaks at 284.8 eV, 285.4 eV, 286.4 eV and 288.8 eV that originate from aliphatic carbon, C–COO, C–O, and COO, respectively.

The fraction of COO was quantified to be in ranges between 8 and 17% of the total carbon, without a clear trend between the different polymers, but with high repeatability between different samples of the same polymer. This fraction is slightly lower than expected (for HDA homopolymers 16.7%, for pure PMMA 20% and for EDA homopolymers 25%). The fraction detected by XPS is, however, also affected by the distribution of the elements inside the thin films. The results here may indicate that carboxyl groups may be enriched inside the film, and oxygen-poor parts

Figure 4.5: (I) IR and (II) C 1s XP spectra of different covalently-bound polymer coatings on zinc, (a) PMMA without cross-linker, (b) PMMA + 25% EDA, (c) PMMA + 50% EDA, (d) PMMA + 25% HDA, (e) PMMA + 50% HDA.
Table 4.1: Polymer film thickness obtained from ellipsometric measurements for PMMA samples with different cross-linker ratios

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA without cross-linker</td>
<td>25 ± 5</td>
</tr>
<tr>
<td>25% EDA</td>
<td>12 ± 2</td>
</tr>
<tr>
<td>50% EDA</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>25% HDA</td>
<td>14 ± 3</td>
</tr>
<tr>
<td>50% HDA</td>
<td>12 ± 3</td>
</tr>
</tbody>
</table>

of the polymer chains may be present directly at the surface. Initiator fragments inside the film may also lower the COO fraction. In all samples after polymerization, the Si 2p peak remains centered at 102 eV, as shown for the VTS-modified surface in Figure 4.2b. This peak position is typical for organosilanes indicating that these structures are still present in an unmodified form after polymerization. In the XP spectra, Zn peaks are absent except for films with a thickness <10 nm, confirming a full coverage of the zinc with polymer on the level of XPS sensitivity (see Figure 4.4).

The thickness of the obtained polymer films was analyzed by ellipsometry. As shown in Table 4.1, increase in the cross-linker fraction results in the reduction of polymer film thickness. This observation is tentatively attributed to a higher rate of quenching of the propagation reaction in case larger amounts of cross-linker are used\textsuperscript{154}. Ellipsometric spectra could be well-described by a simple ambient-film-substrate model, which confirms that the films are not inhomogeneous on the length scale of several 10s of nm.

4.2.2 Model corrosion experiments

In order to study the stability of synthesized silane-bonded PMMA coatings against cathodic delamination, the propagation of a delamination front from a defect filled with 1 M KCl was monitored by SKP measurements. Figure 4.6 shows the SKP potential profile recorded on spin coated PVB, as well as on covalently bound PMMA. Scans were obtained by scanning along the surface from the artificial defect, and show the recorded potential as a function of distance from the defect for different times. In the initial stages of the experiment, the SKP measures the potential of an intact (i.e. non-corroded) polymer/oxide/metal interface all over the sample. However, with time, cathodic delamination is initiated in a humid air atmosphere on both samples as shown in Figure 4.6. Consequently, during passage of a delamination front, two distinct potential levels are observed\textsuperscript{12}. The more negative potential (\(\approx -0.7\) V) indicates actively corroding zinc in the region were the polymer is already delaminated, while the more positive potentials (\(\approx -0.2\) V) indicates an intact polymer/metal interface\textsuperscript{12}. Between these two potentials, a sharp transition region can be observed, which is the position of the delamination front\textsuperscript{12}. The progress of the
4.2. Results and discussion

Figure 4.6: SKP delamination profile of (a) covalently bound PMMA on zinc and (b) weakly bound PVB used for reference purposes, both in air.

delamination front with time \( t \) is plotted in Figure 4.7a for several coatings. Plotting the same results on a double logarithmic scale (Figure 4.7b) enables to determine the exponent \( \alpha \) of the time dependence. While for diffusion controlled processes, the position \( d \) of the delamination front travels as \( d \sim t^{1/2} \) \( (\alpha = 1/2) \), a time dependence as \( d \sim t^1 \) \( (\alpha = 1) \) is expected if a first-order reaction is rate-determining. Alternatively, \( d \sim t^1 \) may indicate migration in a constant static electric field. Here, exponents \( \alpha \approx 1 \) are found, with maximum 5% deviation for all except one portion of a curve, which will be discussed below.

Hence, the delamination rate \( r \) was determined from the slope of a linear fit in Figure 4.7a. The rates for different samples are shown in Table 4.2. Figure 4.7a shows that the progress of the delamination front is inhibited on zinc substrate modified with covalently-bound PMMA without cross-linker \( (r = 0.27 \pm 0.02 \text{ mm h}^{-1}) \), compared to the reference sample with spin-coated PVB \( (r = 11.0 \pm 0.05 \text{ mm h}^{-1}) \).
and spin-coated PVB on VTS-modified zinc \( r = 0.52 \pm 0.02 \text{ mm h}^{-1} \). When changing from humid air atmosphere to humid nitrogen, no cathodic delamination was observed. In this case, the potential remained at the potential of the intact polymer/metal interface. (Attempts to produce PMMA films by spin coating which were not covalently linked but have a thickness comparable to the thickness of the synthesized layers failed.)

![Graph showing delamination front vs. time](image)

**Figure 4.7**: Comparison of the delamination rates for polymer coatings with different cross-linker amounts (a) on a linear scale and (b) on a double logarithmic scale. In the plot (b), two dotted lines show the expected slopes for \( d \sim t \) and \( d \sim \sqrt{t} \), as indicated in the graph.

In order to gain further insight into the effect of network chain length and degree of cross-linking on the stability of these coatings against corrosion in general and against cathodic delamination in particular, additional coatings were synthesized.
Table 4.2: Delamination rates and standard deviations for the different samples, based on linear fits of plots as in Figure 4.7. All samples were covered with PVB, as explained in the experimental section.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Delamination rate / mm h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure PVB</td>
<td>11.2 ± 0.5</td>
</tr>
<tr>
<td>VTS</td>
<td>0.52 ± 0.03</td>
</tr>
<tr>
<td>no cross-linker</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td>25% EDA</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td>50% EDA</td>
<td>0.042 ± 0.004</td>
</tr>
<tr>
<td>25% HDA</td>
<td>0.039 ± 0.003</td>
</tr>
<tr>
<td>50% HDA</td>
<td>0.028 ± 0.004</td>
</tr>
</tbody>
</table>

on VTS-modified zinc substrates with two different cross-linker chain length. The different molar ratios employed should result in a different degree of cross-linking. Delamination was monitored by SKP, and the delamination rates obtained are included in Table 4.2. In one case of the cross-linked samples, namely in the case of coatings containing 50% HDA cross-linker, a $t^1$ behavior is found initially, which at larger times changes to $t^{1/2}$. Such a transition is observed only for this particular type of samples. Overall, the results show a higher rate of delamination for EDA-cross-linked samples compared to HDA-cross-linked samples. That is, polymer coatings with a shorter cross-linker chain length delaminate faster than coatings with a longer chain between the two polymerizable functional groups of the cross-linker. Moreover, an increase in the amount of cross-linker leads to a decrease in the delamination rate. EDA-cross-linked samples delaminate, however, at a similar rate than non-cross-linked samples.

Furthermore, investigation of the samples after a delamination experiment with scanning electron microscopy reveals the growth of crystalline ZnO corrosion products. The growth of zinc oxide/hydroxide structures after cathodic delamination has been shown in the past\cite{12,140}. The corrosion resistance of different coatings was also evaluated by performing linear polarization experiments. Typical Tafel plots obtained for bare zinc and coated zinc are shown in Figure 4.8 (It must be noted that as opposed to the SKP experiments, no PVB coating was present for these experiments.). Corresponding corrosion current rates were calculated from the polarization resistance\cite{130}, and are tabulated in Table 4.3. The highest value of corrosion current were naturally recorded for bare, uncoated zinc. Consequently, zinc oxidation rates (from oxide formation and dissolution) as well as the accompanying cathodic reaction, most likely the oxygen reduction reaction in this system are highest for pure zinc. Overall corrosion currents are lower for coated zinc samples, showing that indeed the coatings have the expected corrosion-inhibiting effect. Comparing the corrosion currents of different samples (Table 4.3) show that all cross-linked coatings exhibits lower corrosion currents than coatings without cross-linking. The
Table 4.3: Corrosion current densities $i_{\text{corr}}$ for differently coated samples in 0.1 M KCl. dec= decade of current. “no cross-linker” refers to non-cross-linked PMMA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\beta_a$ / mV dec$^{-1}$</th>
<th>$\beta_c$ / mV dec$^{-1}$</th>
<th>$R_p$ / $\Omega$ cm$^2$</th>
<th>$i_{\text{corr}}$ / $\mu$A cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>zinc uncoated</td>
<td>104 ± 4</td>
<td>176 ± 3</td>
<td>317 ± 15</td>
<td>89 ± 5</td>
</tr>
<tr>
<td>no cross-linker</td>
<td>105 ± 4</td>
<td>196 ± 8</td>
<td>780 ± 60</td>
<td>38 ± 4</td>
</tr>
<tr>
<td>25% EDA</td>
<td>43 ± 3</td>
<td>161 ± 2</td>
<td>860 ± 30</td>
<td>17 ± 1</td>
</tr>
<tr>
<td>50% EDA</td>
<td>54 ± 2</td>
<td>168 ± 3</td>
<td>1120 ± 30</td>
<td>15.8 ± 0.7</td>
</tr>
<tr>
<td>25% HDA</td>
<td>62 ± 2</td>
<td>150 ± 3</td>
<td>1560 ± 50</td>
<td>12.2 ± 0.6</td>
</tr>
<tr>
<td>50% HDA</td>
<td>58 ± 2</td>
<td>137 ± 3</td>
<td>4200 ± 200</td>
<td>4.2 ± 0.3</td>
</tr>
</tbody>
</table>

Sample with the lowest overall corrosion current is the same that shows the lowest delamination rate. However, the difference between EDA and HDA is not clearly visible in the corrosion currents. Both coatings also inhibit the dissolution as expected, which shows in the lower currents in the anodic branch of the plots in Figure 4.8.

![Figure 4.8: Polarization curves in the form of Tafel plots in 0.1 M KCl for zinc with different coatings, (a) with EDA cross-linker, (b) with HDA cross-linker.](image)

Figure 4.8: Polarization curves in the form of Tafel plots in 0.1 M KCl for zinc with different coatings, (a) with EDA cross-linker, (b) with HDA cross-linker.

The typical Bode plots of the investigated materials after 2 h of immersion are given in Figure 4.9. The 50% HDA cross-linked polymer indicates a prevailing capacitive behavior. The corresponding EIS spectrum shows only one time constant after 2 h of immersion. However, in case of the other samples the phase angle is starting to decrease at lower frequencies, a consequence of the electrolyte ingress into the polymer. As a consequence of the penetrating solution, electrochemical reactions can take place at the metal surface, resulting in the presence of a second time constant in the Bode plots. The first process at high frequencies can be attributed to the coating capacitance and resistance. The second process at low frequencies can be related to the charge-transfer resistance and the electrical double-layer ca-
4.2. Results and discussion

Figure 4.9: Bode plots (top: modulus of impedance $|Z|$, bottom: phase) for the selected polymer systems as indicated in the graph after 2 h of immersion in borate buffer. The straight lines represent the fitted curves of the corresponding sample.

pacitance at the metal/solution interface.\textsuperscript{155} Moreover, based on the decrease of the impedance modulus at lowest frequencies ($10^{-1}$ Hz), a comparison of the protective properties of the selected systems can be made, via the charge transfer resistance. As a tendency, the more hydrophobic HDA cross-linker is granting better protection from water ingress than EDA cross-linker. Higher cross-linker concentrations also slow down the penetration of the electrolyte to the metal surface.

Plasma polymers are ultrathin polymer films which are typically highly cross-linked. Charge transfer/polarisation resistance found here for coatings by free radical polymerization are in similar order of magnitude comparing with literature data on plasma polymers\textsuperscript{156}. Slowest delamination rates found here are of same order as published results for plasma polymers on steel with even lower electrolyte concentration.\textsuperscript{101}

4.2.3 Discussion of the chemistry of cathodic delamination

First, it is obvious that the presence of a coating on metallic zinc reduces the corrosion rates, as it inhibits interfacial electron transfer reactions through blocking transport paths and active sites. Second, a covalently bound coating delaminates considerably slower than a coating which is attached to the surface by van der Waals forces only. It is known that modification of oxide-covered metal surfaces with covalently bound polymers inhibits the oxygen reduction reaction at the polymer/metal interface as a result of a strong chemical bond\textsuperscript{157–159}.

The linear dependence of the delamination front location from the experiment time shows that diffusion (e.g. of oxygen or water through the coating) is not rate limiting\textsuperscript{100}. Indeed, for low oxygen partial pressure, the contribution of ion diffusion to overall transport was reported to be overestimated\textsuperscript{13}. Consequently, the differences observed for delamination rates and corrosion currents between the cross-
linked polymer coatings cannot be explained by differences in transport through the thin polymer films. Likewise, the relatively small differences between the polymer coating thicknesses cannot explain the observed differences, as the thinner coatings with high molar ratios of cross-linkers show lower corrosion currents than the slightly thicker coatings.

The overall amount of hydrophobic groups is one factor contributing to the observed differences between the coatings. Large fractions of HDA in the monomer solution lead to the presence of a large fraction of hydrophobic alkyl chains in the final polymer. EDA as cross-linker on the other hand does not significantly alter hydrophilicity of the polymer layers compared to PMMA. Hydrophobic polymer layers cannot take up as much water as less hydrophobic coatings. Lower availability of the solvent water during the corrosion process is decreasing the corrosion rate and the delamination rate. The coating which is expected to be the most hydrophobic changes to a transport-controlled delamination mechanism at longer exposure.

The behavior of the coatings in linear polarization experiments and in delamination experiments is not the same. Coatings without cross-linker show similar delamination rates as EDA-cross-linked coatings, while their corrosion currents are twice as high. As cross-linked coatings block transport routes in between different polymer chains, they decrease the corrosion current, but not the delamination rate. Delamination rates do overall roughly follow the same trends as observed for the low-frequency impedance modulus, which reflects the charge transfer resistance.

The observed $t^1$-delamination kinetics may be determined by migration of ions in a constant electrostatic potential gradient, or by a first-order chemical reaction. For migration in the electric field, ion flux is proportional to the electric field gradient (e.g. $139^\text{1}$). When comparing the delamination curves (e.g. shown in 4.7), it becomes obvious that the potential difference between active and non-active region is very similar for all polymers. With the lateral resolution used here, the distance above which the potential drop is observed is also quite similar for the different samples. Hence, the differences in delamination rate between the different samples caused by migration in the electric field alone should be rather small. Therefore focus is on the discussion of the chemical reactions as responsible for the observed differences between the coatings.

Considering cathodic delamination, two types of reactions could be rate determining, either the oxygen reduction reaction (ORR), which drives the delamination front, or the deadhesion process, which involves breaking of covalent bonds in the reactions here. It is hard to see why the rate of the ORR should depend on the amount of cross-linker present in the preparation. Instead, the ORR rate, as any rate of an electron transfer reaction, is a sensitive probe of the state of the interface, especially of defects in the layers, i.e. free metal surface which is available to the electron transfer reaction. While it is possible that the presence of the cross-linker in the copolymerization reaction modifies the interface, it is less likely. All surfaces were subjected to identical treatments before polymerization, so the metal(oxide)/silane interface is supposed to be identical. In the actual deadhesion process, several pro-
cesses could potentially occur. It is known that the hydroxide as reaction product of the ORR leads to strongly alkaline conditions in the vicinity of the delamination front. Hydroxide could involve in a number of follow up reactions: (a) in the alkaline dissolution of zinc oxide under hydroxozincate formation according to

$$\text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_4^{2-}, \quad (4.1)$$

or (b) in the alkaline hydrolysis of Si–O bonds under silicate formation according to

$$\text{R}^{(1)}\text{Si(OR)}^{(2)}_3 + 3\text{H}_2\text{O} \rightarrow \text{R}^{(1)}\text{Si(OH)}_3 + 3\text{R}^{(2)}\text{OH}. \quad (4.2)$$

Both reactions are possible at pH $> 11$. Both dissolution of ZnO and hydrolysis of Si-O bonds are not expected to be affected by the presence of cross-linked structures in the polymer film. In both cases, the inorganic part of the metal/polymer interface will dissolve. A further degradation reaction is an alkaline ester hydrolysis of the PMMA under formation of carboxylate and alcohol according to

$$\text{R}^{(1)}\text{COO}^{(2)} + \text{OH}^- \rightarrow \text{R}^{(1)}\text{COO}^- + \text{R}^{(2)}\text{OH}. \quad (4.3)$$

This reaction does, however, not lead to a breakage of the polymer main chain, and hence not to de-adhesion of the complete coating. Alkaline ester hydrolysis would, however, affect the cross-linking, as both cross-linkers link polymer chains via ester bonds. As an alternative to processes involving OH$^-$, radical reactions are other candidates which could lead to the deadhesion of the polymer films. Radical intermediates have been shown to occur in the ORR. Here, only radical reaction can explain all the results without involvement of a complex coupling of polymer degradation and e.g. zinc oxide dissolution. Previous reports have shown a decrease in delamination rate in the presence of radical scavengers.

### 4.3 Summary

Free radical copolymerization of dissolved and surface-bound monomers has been used to synthesize PMMA coatings with thicknesses in the order of 10-20 nm on the industrially relevant metal zinc. Adding certain amounts of cross-linkers enables a systematic variation of the degree of cross-linking in the resulting coatings. The coatings prepared here are covalently linked to the base metal via organosilanes; such coatings show a larger resistance towards cathodic delamination than coatings bound exclusively via van der Waals interactions. The delamination rate decreases to $< 1/10$ only by introducing covalent bonds to the base metal. Introduction of cross-linkers further slows down delamination, with another factor of $\sim 10$ between non-cross-linked PMMA and samples with 50% cross-linker. Comparing the two cross-linkers used in this study, the more hydrophobic HDA yields the lowest delamination rates of all samples investigated in this study, of $0.028 \pm 0.004$ mm h$^{-1}$. 

47
Chapter 5: Delamination kinetics of model PS coatings on zinc bound via organosilanes

5.1 Introduction

The barrier properties of polymer coating against aggressive species like oxygen and water plays a vital role in defining the final corrosion protection properties of a coating\(^2\). The permeability of these species through the coating is defined by the structure and morphology of the protective organic film\(^{117}\). The diffusion of gases like oxygen, nitrogen e.t.c is governed by a diffusion process present in the polymer, as these species hardly interact with the polymer. Therefore, the structural attributes such as holes/defects in a polymer structure could significantly increase the diffusion of oxygen through the coating. On the other hand, permeability of water is strongly governed by the solubility due to strong interaction with the polymer\(^{117}\). It has been shown that although water and oxygen may not be the rate determining step in corrosion, however they are essential for initiation of a corrosion reaction. Water is essential to establish a electrochemical corrosion cell beneath the coating\(^1\) and oxygen is to complete the corrosion reaction\(^{117}\). In particular, close packing of polymer chains and higher fractions of hydrophobic groups leads to enhanced resistance against permeation of water and oxygen\(^{165}\). Moreover, it has been shown that polymers containing stiff chain molecules (such as aromatic rings) tends to significantly reduce the diffusion of water molecules through the polymer chains\(^{166}\).

In the previous chapter, the effect of chemisorbed linear and cross-linked PMMA coatings on the cathodic delamination rate has been studied. PMMA is a aliphatic polymer that has higher chain flexibility when compared to aromatic polymers such as PS. Since aromatic polymers compared to aliphatic polymers exhibits enhanced barrier properties against water and oxygen\(^{117}\), it is expected that they also show enhanced resistance against cathodic delamination process. Hence, the aim of this work is to study the effect of PS polymer, linked via silane bond to the zinc surface, on the cathodic delamination kinetics of a coating. Moreover, cross-linked PS coatings were also synthesized by addition of aliphatic bifunctional molecule during the polymerization reaction.
5.2 Results and discussion

5.2.1 Synthesis of polymer coatings

The modification of zinc substrate with VTS and characterization with IR, XPS and TOF-SIMS were carried out using the synthetic route explained in chapter 4.

After successful functionalization of zinc surface with VTS, PS was grown on top of functionalized zinc surface via thermally initiated free radical polymerization of styrene monomer in presence of AIBN as a thermal initiator (see Figure 5.1). As in the case of free radical polymerization of MMA explained in chapter 4, two fractions of PS polymer were formed. One fraction was covalently bonded to the substrate, due to surface initiated polymerization reaction, while the other fraction was either physisorbed on the surface or present in the solvent phase. The physisorbed polymer was removed by access cleaning with acetone and toluene.

In addition to linear PS polymer, cross-linked PS coatings were synthesized on top of functionalized zinc samples by adding a bifunctional cross-linking molecule at the start of polymerization reaction that leads to cross-linked polymer coatings. The bifunctional molecules used were of different chain lengths (i.e. EDA and HDA).
5.2. Results and discussion

Figure 5.2: IR spectra of different covalently-bound polymer coatings on zinc, (a) PS without cross-linker, (b) PS + 25% EDA, (c) PS + 50% EDA, (d) PS + 25% HDA, (e) PS + 50% HDA.

Table 5.1: FTIR stretching vibration position (cm\(^{-1}\)) of linear and cross-linked PS coatings synthesized on zinc surface based on reference\(^{150}\).

<table>
<thead>
<tr>
<th>Peak Assignment</th>
<th>PS + 25% EDA</th>
<th>PS + 50% EDA</th>
<th>PS + 25% HDA</th>
<th>PS + 50% HDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C-C [s]</td>
<td>1589</td>
<td>1592</td>
<td>1579</td>
<td>1598</td>
</tr>
<tr>
<td></td>
<td>1494</td>
<td>1490</td>
<td>1492</td>
<td>1490</td>
</tr>
<tr>
<td>C-H [s, aromatic]</td>
<td>3060</td>
<td>3060</td>
<td>3058</td>
<td>3062</td>
</tr>
<tr>
<td>CH(_2) [as]</td>
<td>2917</td>
<td>2922</td>
<td>2923</td>
<td>2922</td>
</tr>
<tr>
<td>CH(_2) [ss]</td>
<td>2848</td>
<td>2848</td>
<td>2854</td>
<td>2851</td>
</tr>
<tr>
<td>CH(_2) [bend]</td>
<td>1446</td>
<td>1445</td>
<td>1446</td>
<td>1450</td>
</tr>
<tr>
<td>C=O [s]</td>
<td>-</td>
<td>1737</td>
<td>1737</td>
<td>1731</td>
</tr>
</tbody>
</table>

*s = stretching, ss = symmetric stretching, as = antisymmetric stretching

\(^{150}\)
and were added in different molar ratios (i.e. 25 mol% and 50 mol%) to yield polymer coatings with different morphology and cross-linking densities. Linear and cross-linked polymer coated zinc samples was then characterized by IR and XPS to determine the chemical composition of the surface. Figure 5.2a-e shows the measured IR spectrum on chemisorbed PS coating grafted to zinc substrate via silane bond. The appearance of bands at 1589 cm\(^{-1}\) and 1494 cm\(^{-1}\) is assigned to the aromatic ring stretching arising from the ring structure present in the PS polymer. Moreover, there is an additional band present at around 3060 cm\(^{-1}\) that is assigned to the C-H stretching mode of aromatic ring. Hence, the presence of the aromatic ring stretching modes confirms the successful growth of PS polymer coating on top of the silane modified zinc substrate. In case of cross-linked coatings, the presence of C=O stretching mode at around 1725 cm\(^{-1}\) confirms the presence...
Table 5.2: Thickness of as synthesized linear and cross-linked PS coatings obtained from ellipsometric measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS without cross-linker</td>
<td>15 ± 3</td>
</tr>
<tr>
<td>25% EDA</td>
<td>10 ± 2</td>
</tr>
<tr>
<td>50% EDA</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>25% HDA</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>50% HDA</td>
<td>10 ± 3</td>
</tr>
</tbody>
</table>

of ester functionality that comes from the cross-linking molecule. The detailed assignments of IR spectra is summarized in Table 5.1.

Figure 5.3 shows the high resolution C 1s XPS spectra of chemisorbed linear and cross-linked PS coating grown on zinc substrate. The peak is deconvoluted in to four sub peaks as show in Figure 5.3a-e. C-H peak is assigned at 284.8 eV which arises from the polymer backbone and partially from the impurities present on the surface due to exposure to open air. Carbonate peaks are assigned at 285.4 eV, 286.4 eV and 288.8 eV arises from the presence of acrylate based cross-linker in the polymer coating.

The thickness of the as synthesized polymer coatings was determined by ellipsometry and obtained values are summarized in Table 5.2.

5.2.2 Model corrosion experiments

The stability of these as synthesized chemisorbed linear and cross-linked coatings against cathodic delamination was characterized by SKP. Prior to the SKP experiments, polymerized zinc samples were spin coated with PVB to yield ≈1 µm thick physisorbed polymer film to prevent the immediate spreading of an electrolyte. SKP experiments were performed under similar experimental conditions as carried out for chemisorbed PMMA coatings explained in chapter 4. Figure 5.4 shows the SKP potential profile recorded on spin coated PVB, as well as on covalently bound linear PS coating. The delamination rates were calculated from the plot of progress in delamination front with time and is summarized in Table 5.3. Similarly, the same results were plotted on a double logarithmic scale (see Figure 5.5b) which enables to determine the exponent \( \alpha \) of the time dependence. Delamination rates are initially reaction controlled, while on larger time scales, cathodic delamination process becomes diffusion limited. This phenomenon is attributed to the higher hydrophobicity of PS polymer due to presence of aliphatic chains that exhibits lower water solubility. Hence, on larger times scales, the cathodic delamination process transforms from reaction controlled to diffusion limited process.

Figure 5.4 shows the progress of delamination front for physisorbed PVB coating on zinc as well as for chemisorbed linear PS coating. It is quite evident from the Figure 5.5 that physisorbed PVB coating has very high delamination veloc-
Figure 5.4: SKP delamination profile of (a) covalently bound PS on zinc and (b) weakly bound PVB used for reference purposes, both in air.

...
5.3 Summary

This chapter shows the investigation on the cathodic delamination kinetics of linear and cross-linked PS coatings that are covalently linked to the base metal via organosilanes. These ultrathin coatings were synthesized on top of modified zinc substrate via thermally initiated free radical polymerization of styrene. The results show that the chemisorbed PS coatings exhibits slower delamination rates than physisorbed PVB coating. Moreover, addition of aliphatic cross-linking agents does not leads to a significant reduction in the cathodic delamination rates. In particular, PS coatings cross-linked with EDA exhibits slower delamination rates than the coatings cross-linked with HDA. The addition of the cross-linker with longer aliphatic chain (HDA) effects the close packing of aromatic groups that are present in the PS polymer and hence, leads to lower resistance against cathodic delamination.
Chapter 6: Delamination kinetics of model PMMA coatings bound to zinc via ester linkage

6.1 Introduction

Polymer coatings with specific functionalities are often used in industrial polymer coatings because of their desirable structural and interfacial performances. In particular, carboxylic functionalities has gained much attention due to their importance in understanding the fundamental adhesion mechanisms at polymer/metal interfaces\(^\text{94,167}\). The bonding properties at polymer/metal interface is affected by several factors. The most crucial factor is the end functional group that leads to a covalent bonding between polymer and metal. Moreover, the metal substrate is often pretreated before application of a polymer coating in order to enhance the adhesion strength and improve the corrosion performance\(^\text{168}\). It has been shown that carboxylic functionality can attach to the zinc oxide surface via coordinative bonding\(^\text{167,169}\).

In the chapter 4 and 5, it has been demonstrated that covalently adhered PMMA and PS coatings linked to zinc substrate via silane bond leads to enhanced protection of polymer coatings against cathodic delamination. Moreover, it was also shown that the morphology and hydrophilicity of polymer coating also plays a role in defining the deadhesion properties of a coatings due to different barrier properties against aggressive species like oxygen and water. Previous studies have shown that the adhesion strength between metal and polymer is determined by the functional groups that are present in polymer which makes covalent bonding with the surface hydroxyl groups of zinc\(^\text{95,115}\). Therefore in this chapter, the cathodic delamination kinetics of linear and cross-linked PMMA coatings that are attached to the metallic substrate via ester linkage is investigated. In order to obtain polymer coating bound to zinc via ester linkage, the zinc substrate was functionalized with acryloyl chloride instead of VTS.
Chapter 6. PMMA model coatings bound via ester linkage

6.2 Results and discussion

6.2.1 Surface modification

Initially, zinc substrate was treated with acryloyl chloride that leads to ester linkage at metal/organic interface. As shown in Figure 6.1, the functionalization reaction was carried out at room temperature in THF and in the presence of triethylamine. Triethylamine acts as a buffer and reacts with the hydrochloric acid (HCl) produced during the reaction forming triethylammoniumchloride which precipitates and is not active in the reaction anymore. As this is an equilibrium reaction, removal of HCl is necessary for the completion of the reaction otherwise back reaction will occur, which results in the cleavage of ester bond by the HCl produced during the reaction. Successful functionalization could be proved by IR, XPS and TOF-SIMS experiments. Figure 6.2a shows the IR spectrum of acryloyl chloride modified zinc substrate. The bands at 2924 cm$^{-1}$ and 2865 cm$^{-1}$ are assigned to anti symmetric and symmetric stretching modes of CH$_2$, respectively\textsuperscript{150}. Moreover, the presence

Figure 6.1: Scheme of the surface modification steps carried out in this chapter.
of band centered at 1725 cm$^{-1}$ confirms the presence of C=O group. The formation of covalent bonding between zinc and acryloyl chloride can be confirmed by the appearance of the band at around 1600 cm$^{-1}$ and 1440 cm$^{-1}$ that is assigned to the antisymmetric and symmetric stretching vibrational modes of CO$_2$ \textsuperscript{167,170}. Presence of both symmetric and antisymmetric stretching modes indicates that carboxylate bonds are inclined at a certain angle with respect to the surface. Figure

![Figure 6.2: (a) IR spectrum of acryloyl chloride modified zinc. (b) C 1s region of the XP spectrum of acryloyl chloride modified zinc.](image)

6.2b shows the high resolution C 1s XP spectra. The peak is decomposed into C-C/C-H (284.8 eV), C-O (286.4 eV) and CO$_2$ (289.1 eV) sub peaks. To further verify the successful modification of zinc surface with acryloyl chloride, TOF-SIMS measurements were performed. Figure 6.3 depicts the positive TOF-SIMS spectra measured at the interfacial region of modified zinc substrate with assignment of main
ions. The presence of the fragment ZnOCH\(^+\) is an indicative of presence of ester linkage between polymer and a metal substrate. Moreover, the ion pattern of the fragment ZnOCH\(^+\) should reflect the isotopic abundance of the elements present; the observed distribution is in close agreement to the calculated distribution.

The growth of linear and cross-linked polymer coatings on functionalized zinc surface that is covalently bonded to the anchoring molecule was achieved by using similar synthetic route explained in chapter 4. To verify the successful growth of polymer on functionalized zinc substrate, the polymerized samples were characterized with IR and XPS. Figure 6.4 I demonstrates the IR spectra measured on as synthesized PMMA coatings. The presence of peak at around 1725 cm\(^{-1}\) is assigned to C=O and that confirms the presence of PMMA. Moreover, the increase in the intensity of C-H stretching bands at around 2960-2850 cm\(^{-1}\) also depicts the presence of long aliphatic polymer chains. The detailed assignment of IR peaks are summarized in Table 6.1.

Moreover, XP spectra (Figure 6.4 II) of polymer-modified samples show the expected C 1s and O 1s peaks. The high resolution C 1s spectrum can be decomposed in to four distinct peaks at 284.8 eV, 285.4 eV, 286.4 eV and 288.8 eV that originate from aliphatic carbon, C–COO, C–O, and COO, respectively.

Figure 6.3: SIMS showing the isotope distribution of ZnOCH\(^+\) fragments from the surface of acryloyl chloride modified zinc. Expected isotope distribution is shown as vertical lines (|) ca. 0.3 amu below the experimental peak.
6.2. Results and discussion

Figure 6.4: IR and C 1s XP spectra of different covalently-bound polymer coatings on zinc, (a) PMMA without cross-linker, (b) PMMA + 25% EDA, (c) PMMA + 50% EDA, (d) PMMA + 25% HDA, (e) PMMA + 50% HDA. Dotted red lines are indicating the area of interest in both IR and XP spectra.

Ellipsometry was used as an analytical tool to determine the thickness of as synthesized linear and cross-linked PMMA coatings. The obtained polymer thickness values are summarized in Table 6.2.

6.2.2 Model corrosion experiments

Model corrosion experiments were performed as explained in chapter 4. Figure 6.5 demonstrates the SKP potential profiles measured over zinc sample that is modified with PMMA (having a ester linkage with the substrate) and coated with PVB along with the physisorbed PVB coated zinc.

It is shown in Figure 6.6a that the progress of the delamination front is fastest in the case of spin coated PVB, while the progress of the delamination front is inhibited in case of chemically modified zinc samples. The increased delamination velocity of
Table 6.1: FTIR stretching vibration position (cm\(^{-1}\)) of AC and different PMMA coatings with and without cross-linker synthesized on zinc surface based on reference\(^{150}\)

<table>
<thead>
<tr>
<th>Peak Assignment</th>
<th>AC</th>
<th>PMMA + 25% EDA</th>
<th>PMMA + 50% EDA</th>
<th>PMMA + 25% HDA</th>
<th>PMMA + 50% HDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3) [as]</td>
<td>2993</td>
<td>2992</td>
<td>2987</td>
<td>2984</td>
<td>2993</td>
</tr>
<tr>
<td>CH(_3) [ss]</td>
<td>2956</td>
<td>2953</td>
<td>2948</td>
<td>2954</td>
<td>2948</td>
</tr>
<tr>
<td>CH(_2) [as]</td>
<td>2924</td>
<td>2917</td>
<td>2922</td>
<td>2923</td>
<td>2922</td>
</tr>
<tr>
<td>CH(_2) [ss]</td>
<td>2865</td>
<td>2848</td>
<td>2848</td>
<td>2854</td>
<td>2851</td>
</tr>
<tr>
<td>CH(_2) [bend]</td>
<td>1455</td>
<td>1440</td>
<td>1445</td>
<td>1460</td>
<td>1446</td>
</tr>
<tr>
<td>C=O [s]</td>
<td>1730</td>
<td>1733</td>
<td>1738</td>
<td>1737</td>
<td>1736</td>
</tr>
<tr>
<td>C=C [s]</td>
<td>1635</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>COO(^-) [as]</td>
<td>1590</td>
<td>1587</td>
<td>-</td>
<td>1578</td>
<td>1600</td>
</tr>
<tr>
<td>C-O [stretching]</td>
<td>1150</td>
<td>1149</td>
<td>1153</td>
<td>1153</td>
<td>1160</td>
</tr>
</tbody>
</table>

*s = stretching, ss = symmetric stretching, as = antisymmetric stretching

Table 6.2: Polymer film thickness obtained from ellipsometric measurements for linear PMMA samples along with coatings having different cross-linker ratios bounded to zinc via ester linkage.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA without cross-linker</td>
<td>25 ± 6</td>
</tr>
<tr>
<td>25% EDA</td>
<td>14 ± 3</td>
</tr>
<tr>
<td>50% EDA</td>
<td>13 ± 3</td>
</tr>
<tr>
<td>25% HDA</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>50% HDA</td>
<td>18 ± 6</td>
</tr>
</tbody>
</table>

PVB coated zinc could be explained by the weak van der Waals interaction forces at polymer/metal interface.

In order to gain further insight into the effect of network chain length and degree of cross-linking on the stability of these coatings against cathodic delamination, additional coatings were synthesized on zinc substrates with different cross-linker chain length and degree of cross-linking. Following a similar experimental procedure, these cross-linked polymer coatings were exposed to delamination experiments and progress of cathodic delamination was tracked by SKP. Figure 6.6 shows the position of delamination front with respect to time for coatings cross-linked with EDA and HDA together with different degree of cross-linking. When comparing the delamination rates of EDA and HDA cross-linked PMMA, it can be clearly seen that rate of cathodic delamination is fast on a coatings cross-linked with EDA compared to HDA cross-linked polymer coatings. This could be explained by the fact that
6.2. Results and discussion

Figure 6.5: SKP delamination profile of (a) covalently bound PMMA on zinc and (b) weakly bound PVB used for reference purposes, both in air.

Table 6.3: Delamination rates and standard deviations for the different samples, based on linear fits of plots as in Figure 6.6. All samples were covered with PVB, as explained in the experimental section.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Delamination rate / mm h(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure PVB</td>
<td>11.2 ± 0.5</td>
</tr>
<tr>
<td>no cross-linker</td>
<td>1.32 ± 0.1</td>
</tr>
<tr>
<td>25% EDA</td>
<td>0.67 ± 0.04</td>
</tr>
<tr>
<td>50% EDA</td>
<td>0.55 ± 0.04</td>
</tr>
<tr>
<td>25% HDA</td>
<td>0.44 ± 0.06</td>
</tr>
<tr>
<td>50% HDA</td>
<td>0.25 ± 0.03</td>
</tr>
</tbody>
</table>

EDA has a shorter chain length, which leads to a polymer network structure where chains mobility is hindered and has increased voids/pore in a coating. Moreover, due to shorter aliphatic chain length, it leads to coatings with lower hydrophobicity. Hence, the EDA cross-linked coatings exhibits lower resistance against diffusion of water/oxygen and this eventually increases the oxidative degradation of the polymer/metal interface. Moreover, increasing the cross-linking density by increasing the amount of EDA from 25 mol% to 50 mol% results in deceleration in the degradation rate of the interface as a result of polymer network with high degree of cross-linking between the polymer chains. Thus, there is less free volume available for oxygen and water molecules to diffuse through the network structure, which further reduces the rate of oxygen/reduction reaction in the humid air atmosphere.

On the other hand, HDA has a longer aliphatic chain length which makes the resulting polymer structure more hydrophobic, dense and flexible. Consequently diffusion of water through the polymer network structure is inhibited and thus, progress of delamination front is slowed down. Similarly, increase in the concentration of
Chapter 6. PMMA model coatings bound via ester linkage

Figure 6.6: Comparison of the delamination rates for polymer coatings with different cross-linker amounts (a) on a linear scale and (b) on a double logarithmic scale. In the plot (b), two lines show the expected slopes for $d \sim t$ and $d \sim \sqrt{t}$, as indicated in the graph.

HDA from 25 mol% to 50 mol% results in further deceleration in the degradation rate of the interface as a result of increased hydrophobicity of the polymer.

6.3 Summary

Linear ultrathin PMMA coatings that are covalently bonded to zinc/oxide surface via ester linkage were synthesized by thermally initiated copolymerization reaction. The results yields that covalently grafted PMMA coating lead to significant inhibition in cathodic delamination rate due to enhanced adhesion forces at polymer/metal interface. Furthermore, addition of the cross-linker leads to the deceleration in the delamination rate as a result of denser polymer network structure and reduced number of defects/pores in the coating. However, delamination rates of EDA cross-linked polymer coatings are higher in comparison to HDA cross-linked samples. Higher concentration of EDA results in the network structure with higher hydrophilicity (compared to HDA), which leads to higher water uptake through the polymer coating. On contrary, cross-linker with longer chain length (HDA) shows enhanced resistance against cathodic delamination process due to higher hydrophobicity of polymer coating.
Chapter 7: Comprehensive discussion on cathodic delamination of PMMA & PS with different surface linkage

The presence of a polymer coating on metallic zinc leads to reduction in the corrosion rates, by inhibiting interfacial electron transfer reactions through blocking diffusion paths and active sites. The nature of bonding between polymer and metal also plays a role in defining the final rates of cathodic delamination. In particular, polymer coatings bound to metallic surface via covalent bonding leads to considerable reduction in the corrosion rates in comparison to coatings that are physisorbed to the substrate material. It has been shown that modification of oxide-covered metal surfaces with covalently bound polymers inhibits the oxygen reduction reaction at the polymer/metal interface as a result the strong chemical bond.\textsuperscript{157–159}

In this work, PMMA and PS coatings with different cross-linking densities that are bound to zinc substrate via silane and ester linkage has been synthesized via free radical polymerization and their cathodic delamination behavior is monitored with SKP. The obtained delamination rates are summarized in Table 7.1. It can be seen that the delamination rate is highest for the reference sample that was only coated with PVB. This fast delamination rate of PVB is a result of weak van der Waals interaction with the substrate material. Now, comparing the delamination rates of chemisorbed polymers, PS coatings that are bound to zinc via silane linkage has the lowest, while the ester bonded PMMA coatings has the highest delamination rates.

In order to explain the differences in the delamination rates between these chemisorbed coatings, the factors which could play a role in the cathodic delamination process have to be considered. These factors are the nature of chemical bonding at polymer/metal interface, overall amount of hydrophobic groups in a coating, and morphology of the polymer itself. Considering the delamination rates of PMMA polymer bonded to zinc via silane and ester linkage, there is a quite significant difference in the delamination rates for both the coating systems. In particular, the linear PMMA coating bonded to zinc via ester linkage delaminate faster by the factor of almost 10 then PMMA bound to zinc via silane linkage. The possible explanation for the lower resistance against cathodic delamination for ester bound PMMA coating is the nature of ester bond itself. Ester linkage is quite susceptible to alkaline hydrolysis and as cathodic delamination process leads to high alkaline pH at the metal/polymer interface, this leads to rapid breakage of metal/polymer
Chapter 7. Comprehensive discussion on cathodic delamination

chemical bond. The alkaline hydrolysis of ester linkage is shown in the equation below,

\[ R^{(1)}-\text{COO}^-R^{(2)} + \text{OH}^- \rightarrow R^{(1)}-\text{COO}^- + R^{(2)}\text{OH}. \]  

(7.1)

Moreover, cross-linked PMMA coatings bound to zinc via ester and silane linkage leads to further reduction in the cathodic delamination rates. It is obvious that the this larger resistance against the delamination rate is not due to the nature of chemical bond, as the bond with the metallic substrate remains the same for both linear and cross-linked polymers. As can be seen from Table 7.1, the cross-linking of PMMA coatings leads to reduction in the rate of cathodic delamination for both silane and ester bonding. This could be explained by the fact that cross-linking of the coating leads to denser polymer structures, with increased number of ester linkage between the polymer chains. Due to significantly increased number of cross-linking between the polymer chains, the degradation of polymer via ester hydrolysis takes more time. Consequently, the overall degradation process of a polymer coating is slowed down.

Now, if we look at the delamination rates of linear PMMA and PS coatings bound to zinc via silane linkage, PS coatings show enhanced resistance against cathodic delamination. This inhibition in the delamination velocity could be attributed to higher hydrophobicity and dense packing of polymer chains due to presence of aromatic rings in the PS polymer. It has been shown that dense packing of polymer chains exhibits superior barrier properties against aggressive species such as oxy-

Figure 7.1: Comparison of delamination rates of chemisorbed linear PS and PMMA polymer coatings.
Figure 7.2: Comparison of delamination rates of chemisorbed 50% EDA cross-linked PS and PMMA polymer coatings.

gen and water which are the primary cause of initiation of corrosion reaction. While on the other hand, PMMA polymer is less hydrophobic due to presence of hydrophillic groups. Hydrophobic polymer layers cannot take up as much water as less hydrophobic coatings. This lower availability of the solvent water during the corrosion process leads to reduction in the corrosion rate and the delamination rate. Moreover, when comparing the delamination rates of cross-linked PMMA and PS coatings, there is not a significant difference. This can be again explained by the morphology and hydrophobicity of polymer chains. Although, the addition of aliphatic cross-linking agents to the PS chains leads to increased cross-linking between polymer chains, however, they effect the close packing of aromatic rings that are present in the polymer chain and increases the hydrophilicity of the coating due to presence of hydrophillic groups in the cross-linking molecule. Hence, there is no significant reduction in the cathodic delamination rate of cross-linked PS coatings. On the other hand, cross-linking of PMMA coatings leads to denser polymer network that has enhanced barrier properties against diffusion of aggressive species (independent of surface linkage) like oxygen and water leading to higher resistance against cathodic delamination.

The coatings prepared here via a wet chemical process lead to similar delamination rates, corrosion current densities and charge transfer resistance values as plasma polymers prepared by a gas phase process. Plasma polymers, on the other hand, are ultrathin polymer films which are typically highly cross-linked. Charge transfer/polarization resistance are in similar order of magnitude comparing with
Table 7.1: Delamination rates and standard deviations for the different samples. All samples were covered with PVB, as explained in the experimental section. Sumarizes Tables 5.3, 4.2, 6.3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Delamination rate / mm h(^{-1})</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PS (silane linkage)</td>
<td>PMMA (silane linkage)</td>
</tr>
<tr>
<td>no cross-linker</td>
<td>0.05 ± 0.005</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td>25% EDA</td>
<td>0.048 ± 0.02</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td>50% EDA</td>
<td>0.023 ± 0.005</td>
<td>0.042 ± 0.004</td>
</tr>
<tr>
<td>25% HDA</td>
<td>0.036 ± 0.005</td>
<td>0.039 ± 0.003</td>
</tr>
<tr>
<td>50% HDA</td>
<td>0.039 ± 0.003</td>
<td>0.028 ± 0.004</td>
</tr>
</tbody>
</table>

literature data. Also, slowest delamination rates found here are of same order compared to published results for plasma polymers on steel\(^{101}\). Hence, the coatings prepared here via a wet chemical process are comparable to plasma polymers prepared by a gas phase process.

Delamination rates are reaction-controlled for the PMMA coating systems, investigated here, as shown by the \(t^1\) dependence. In particular, diffusion limitation can be excluded, as this would lead to a \(t^{1/2}\) dependence. Because delamination rates depend on the presence of cross-linkers and the degree of cross-linking. Therefore, the rate-limiting reaction must be related to the polymer of the coating. This observation rules out alkaline zinc oxide dissolution and siloxane/ester bond hydrolysis as sole reactions leading to de-adhesion. Radical reactions as side reactions of the oxygen reduction can explain the observed trends in delamination rate with variation of interface composition. On the other hand, delamination rates are partially diffusion limited on larger time scales for silane bound PS coatings. This diffusion limited dependence is attributed to the higher hydrophobicity of PS coating that shows enhanced resistance against permeation of water and oxygen. Hence, over time the cathodic delamination process for silane bound PS coatings becomes diffusion limited. In summary, delamination mechanisms discussed above is not centered around radical reactions, needs to involve an unlikely coupling by an unknown mechanism between alkaline dissolution of inorganic surface linkages and polymer degradation. The situation encountered in this work is significantly different from the situation in a previous work, were a larger cross-linker amount was found to lead to higher delamination rates in latex polymers because of the increase in interfacial free volume\(^{50}\). Interfacial free volume can form in significant amount in coatings which form by coalescence of latex particles, but is less likely to occur in significant amount in coatings prepared directly by free radical polymerization, as used here. Especially, if interfacial free volume forms, its relation to the cross-linking is not straightforward.
Chapter 8: Study of polymer coating delamination kinetics on zinc modified with zinc oxide of different morphologies

8.1 Introduction

Industrially prepared material surfaces often possess complex morphologies and topographies. Moreover, Zn is always covered with a thin oxide layer, which determines its adhesion to the polymer\textsuperscript{167,171,172}, which is related to its resistance against corrosion. Previous studies have shown that interfacial oxide chemistry plays an important role in adhesion between polymer/metal interfaces. In particular, tailoring the hydroxyl/oxide ratio could lead to the enhancement in the adhesion at polymer/oxide/metal interface\textsuperscript{169}. The native oxide differs in its electronic structure substantially from the crystalline oxide, especially due to the presence of intra-gap states, which may affect adhesion properties\textsuperscript{173,174}. Naturally, the thickness of the oxide films depends on the electrochemical polarization and atmospheric conditions\textsuperscript{175,176}. The dissolution kinetics of ZnO under the conditions of cathodic delamination may, however, also be a crucial factor when determining the rate of delamination.

ZnO itself has become an interesting functional materials in a number of areas, e.g. for application in LEDs\textsuperscript{177}, solar cells\textsuperscript{178}, catalysis\textsuperscript{179}, and nano-sensing\textsuperscript{180}. For most of these applications, micro- or nanostructured surfaces, or small particles are used, where 'small' refers to size parameters below 10 $\mu$m. The properties of micro- and nanostructured ZnO can be affected via control of size and shape\textsuperscript{181,182}. Therefore, a variety of different crystal shapes has been synthesized, ranging from rods/tubes\textsuperscript{86}, belts\textsuperscript{183}, spheres\textsuperscript{184}, to more complex ones like urchins\textsuperscript{185}, flowers\textsuperscript{186}, twin-plates\textsuperscript{187} and pine trees\textsuperscript{89}.

In corrosion protection, the formation of a layer of protective corrosion products on a surface is crucial\textsuperscript{120,121,188}. By deposition of artificial corrosion products on the

\textsuperscript{*}This chapter contains results published as a scientific article:

surface of steel and galvanised steel, the effect of oxides on the oxygen reduction was recently investigated\textsuperscript{188}. This chapter follows a similar idea: ZnO particles with different shapes are deposited on Zn surfaces, and delamination of a model polymer coating is investigated. ZnO crystals of different sizes and shapes (determining overall surface morphology) exhibit different stability towards wet etching in a basic medium, as occurs during cathodic delamination. ZnO dissolution in an alkaline medium has shown to take place at crystal edges\textsuperscript{189}. Consequently, the rate of delamination of a polymer coating should be affected by the oxide surface on top of the zinc coating. A test of this hypothesis is subject of this chapter. Therefore, spherical, rod-shaped and twin-plate-shaped ZnO particles have been synthesized via a sol gel route, and deposited on a metallic Zn substrate. Subsequently, poly(vinyl butyral) (PVB) coatings, as a model for weakly bound polymers on the zinc, have been deposited, and the delamination kinetics was studied in a humid air atmosphere by scanning Kelvin probe (SKP) measurements.

\section*{8.2 Results}

Different microstructures with a certain distribution in size and diameter of the ZnO particles were grown on polished Zn sheet using the hydrothermal technique described above. Figure 8.1 shows the SEM images of twin-plate-shaped (a), rod-shaped (b) and spherical (c) ZnO microstructures precipitated on the Zn sheet substrate. Rod-like structures were synthesized without any surface capping agent, due to the tendency of $c$-axis growth of ZnO\textsuperscript{91}. To obtain other morphologies of ZnO, gelatin and sodium citrate were used for selective protection of one surface. The detailed growth mechanism of twin-plate-shaped ZnO has been discussed in\textsuperscript{187,190}, while the respective mechanism for growth of spherical particles is described in\textsuperscript{184,191}. By varying the growth time and concentration of the surface protecting agents, the size and morphology of the ZnO microstructure can easily be varied.

XRD data, also shown in Figure 8.1, confirms the crystalline nature of the produced ZnO particle-covered surfaces. Comparing the relative intensity ratios of the different ZnO peaks to powder diffraction file No. 00-005-0664 for ZnO shows slight deviations. The most prominent peak is in all cases the 101 peak, though its intensity compared to other peaks in all patterns in this work is higher than in the reference data. On the other hand, the second most intense 100 peak from the reference data is less prominent in the data obtained here. While the patterns for spheres and twin-plates are quite similar, the rod’s pattern shows only a small intensity of the 100 peak, but a substantial 002 peak. There is clearly some preferential growth direction, the overall deviations from the powder data does not indicate a strong dominance of one direction, as would be expected for $c$-axis growth on surfaces\textsuperscript{91}. While there is some evidence for $c$-axis growth in the rod-shaped particles, in all cases the patterns are dominated by the 101 peak, belonging to one of the stable non-polar surfaces of ZnO\textsuperscript{91,192}. Figure 8.2 shows averaged SKP potential scans of the delamination experiments of PVB coatings on Zn and Zn modified with ZnO.
8.2. Results

Figure 8.1: SEM micrographs and XRD patterns of grown ZnO structures on metallic zinc. Left panel: SEM images of (a) ZnO twin plates, (b) ZnO rods, of different morphologies. Initially, SKP measures a potential of the intact polymer/oxide/metal interface. However, with time, cathodic delamination is initiated in a humid air atmosphere on all the samples, as can be seen in Figure 8.2. The progress of the delamination front with time is plotted in 8.3 for three representative examples from each surface morphology, and the slope of a linear fit was determined. This slope is discussed as delamination velocity below. It is evident from Figure 8.3 that progress of the delamination front is by far fastest for PVB on Zn without particles, where a delamination rate of $\approx 11 \text{ mm h}^{-1}$ is observed. The statistical error for all delamination rates reported in this work, including those on the surface with spherical, twin-plate-shaped and rod-like particle, is 0.05 mm/h, which was obtained as the standard deviation from three samples treated according to the same scheme. The actual uncertainty is likely to be higher, due to systematic errors and uncertainties in readout and sample preparation. While on the modified surfaces, thick layers of ZnO microstructures are present, the untreated Zn possesses only its native oxide layer. The observed strong reduction in delamination rate may
therefore have two origins. First, it may be related to an inhibition of the oxygen reduction reaction (ORR), as was observed after deposition of simonkolleite corrosion products on Zn\(^{188}\). Second, the deposited thick layer may protect longer Zn against dissolution, as the ZnO layer needs more time to dissolve under the alkaline conditions present after the delamination front compared to the thin native oxide. It is also important to note that during delamination process, reprecipitation, i.e. formation of zinc hydroxide from solution, takes place, which does not passivate the surface due to porous nature of the film formed\(^{193,194}\).

Now, focusing on the delamination rates of the different ZnO-modified samples, namely containing ZnO spheres, rods, or twin-plates (Figure 8.3), a clear difference between the different surface morphologies is observed. Delamination velocity of cathodic delamination is slowest in the case of deposited ZnO spheres, where it is \(\approx 0.2 \text{ mm h}^{-1}\), while it is fastest on ZnO twin-plate samples with \(\approx 2 \text{ mm h}^{-1}\). Rod-shaped structures show a rate of \(\approx 1 \text{ mm h}^{-1}\), i.e. in between spheres and twin plates.

For all three different morphologies, a reduction in the ORR activity is expected.
Previous studies have shown that ZnO dissolution in an alkaline medium (as present under the conditions here in the passing of the delamination front) takes place at crystal step edges.\textsuperscript{189,195} Macroscopically, a sphere has a smooth surface, without sharp edges and corners, which may explain the particularly low delamination rates on surfaces covered with spherical particles. Sharp corners are present in the case of rod-like and twin-plate structures. From the crystal structure of ZnO, one expects, after typical c-axis growth, the top and bottom of the cylinder to be terminated with a polar (0001) surface, while the sides should be terminated with the lower energy non-polar [e.g. (1010) or (1011)] surface.\textsuperscript{91,192} Consequently, twin plates are expected to have the highest fraction of polar surfaces, while this fraction is reduced in rod-shaped crystals. This difference is reflected in the faster dissolution of the twin-plate covered Zn, compared to rod-covered Zn. The actual surface termination of the spherical particles is not intuitively obvious. Attempts to conclude the orientation of the surfaces from the XRD data shown in 8.1 may be misleading, as this shows the predominant crystal growth direction perpendicular to the surface, which is not necessarily the decisive growth direction. As the surface of a spherical particle is, however, homogenous, one should expect a non-polar surface with defects to adjust in the curvature. These defects are, however, obviously not those needed...
to facilitate dissolution. Kinks and edges on the other hand must be present on the
twin plates and rod, and are obvious sites for start of oxide dissolution under basic
pH. Therefore, the cathodic delamination process is accelerated on ZnO rods and
twin-plates in comparison to spheres.

Figure 8.4: SEM micrographs after the delamination of PVB from (a) ZnO twin-
plate-covered surface and (b) ZnO rod-covered surface.

A second factor which needs to be considered is the availability of surface regions
which are not covered by μm thick oxides. In these regions, oxygen has easy access
to the metal, and the rate of the ORR is therefore faster. For a detailed analysis
of the importance of this effect, however, a detailed study of the interface between
oxide and metal is needed, which is rather difficult to perform. An inspection of the
surfaces after delamination also points to the importance of the oxide dissolution.
SEM images after the cathodic delamination experiment are shown in Figure 8.4.
All the twin-plate structures have been dissolved. Rod-like structures have also
been destroyed, however, the final morphologies resemble rods. Comparison to the
initial morphologies (see Figure 8.1) points to the importance of oxide dissolution
in determining the rate of cathodic delamination.

Two more potential factors of influence on the delamination rate, though through
evidence here considered as not decisive, shall be discussed, (a) the adsorption of
the capping agent and (b) the effect of the overall amount of ZnO in the interface,
i.e. the layer thickness. Organic capping agents have been used for the synthesis of
8.3 Summary

The deposition of ZnO on Zn substantially decreases the delamination rate of polymer coatings on top. The morphology of ZnO plays a crucial role in the determination of the delamination kinetics, with a factor of 10 between the lowest (spherical particle) and highest (twin-plate-shaped particle) delamination rates. A comparison of the surface morphologies before and after the delamination experiments shows that dissolution of the oxide in the interfacial region occurs. The kinetics of delamination is likely determined by the nature of the dominating surface termination of ZnO. These results suggest that a careful control over surface morphologies in a pretreatment-like process offers the chance to significantly increase resistance of polymer-coated galvanized steel towards cathodic delamination.
Chapter 9: Sequential growth of zinc oxide nanorod arrays via a corrosion process

9.1 Introduction

Amongst the big challenges in semiconductor photocatalysis is to tune the bandgap, defect levels and morphology of the catalyst for efficient use of a large part of the visible spectrum, in particular the red fraction of light, to catalyze chemical reactions. TiO$_2$ has been so far the most popular material of study as photocatalysts, e.g. in different nanostructures. A particular important application of semiconductor photocatalysis is the decomposition of organic substances in water via aerobic photooxidation, a potential route to remove persistent pollutants. Using UV light, large conversions in decomposition of an organic dye model pollutant have been achieved recently. For decomposition of organic substances, a number of different materials are currently investigated, including low-cost, non-toxic ZnO. Its band gap at UV photon energies can be modified by crystal strain. While application with UV light is straightforward, more current focus is towards extending the operational range towards visible light. In this regard, most approaches extend the ZnO light absorption from the UV into the blue part of the visible. Alternatively, metal nanoparticles can be conjugated to ZnO. Supported catalysts with large surface areas can conveniently be realized as ZnO nanorod arrays. Consequently, developed synthesis methods include chemical vapour deposition, laser decomposition of a suitable precursor, vapour-liquid-solid growth, pulsed laser deposition, a flame transport method, template based methods, solvothermal techniques, and solution phase approaches. Synthesis can be interfaces with lithographic techniques for regular patterning. All aforementioned preparation techniques either require the use of sophisticated instrumentation, or elevated temperature, with nanorods growing in parallel over the sample area. Besides photocatalysis, other applications of ZnO nanorod arrays...
include gas sensing \cite{217,221}, refractive index sensing \cite{60}, water splitting \cite{222}, antibacterial coatings \cite{223}, and solar cells \cite{58,59}. Corrosion processes may also be used to synthesize nanostructured materials \cite{224}. Here, a strategy for sequentially fabricating highly oriented, 1D ZnO nanorod arrays over large areas on metallic zinc via cathodic delamination of a polymer coating using aqueous KCl at room temperature has been reported. Moreover, it has been demonstrated that the ZnO nanorods mediate the photo-degradation of the organic dye methyl orange under illumination with red light.

9.2 Results

9.2.1 Structure and morphology

ZnO nanorods were grown for typically 6-8 h (maximum 15-18 h) by coating a zinc substrate with poly(vinylbutyral) (PVB), subsequently preparing a defect in the polymer coating, and exposing the defect to a drop of 0.1 M aqueous KCl (unless noted otherwise) at room temperature. The structure and morphology of ZnO nanorods grown over a zinc substrate were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figure 9.1). The SE micrographs demonstrate that well-ordered ZnO nanorods grow densely and uniformly over large areas (Figure 9.1a and 9.1b). Nanorod growth was observed over the full sample, typically 1 cm$^2$, up to sizes of 4 cm$^2$, in the samples used here. Nanorod diameters range between 20-70 nm (Figure 9.1a). Diameters were also verified by tapping mode atomic force microscopy (AFM, Figure 9.1e). The diameter of the ZnO nanorods observed by AFM is slightly higher than observed in SEM images. This difference results from the tip convolution due to the high aspect ratio of ZnO nanorods \cite{225}. The relatively flat top surfaces show that the surface is rather smooth and grown nanorods have similar lengths. The length was found to be 800-1000 nm from scanning TEM (STEM) images of single nanorods detached from the ZnO nanorods array (Figure 9.1c). The lattice planes of the hexagonal nanorods can be clearly seen in the high resolution TEM image (HRTEM) from a single nanorod (Figure 9.1d), from which the selected-area diffraction (SAED) pattern (inset in Figure 9.1d) proves the crystalline nature with a (0001) growth direction.

The crystalline nature of the formed ZnO over the complete sample area is verified by X-ray diffraction (XRD) (Figure 9.1f). In addition to metallic zinc peaks arising from the substrate, the sharp (002) peak of ZnO indicates the highly preferential growth of ZnO nanorods along the $c$-axis \cite{91}.

X-ray photoelectron spectroscopy (XPS; Figure 9.2a), energy dispersive X-ray microanalysis (EDX) measurements (Figure 9.2b) and Raman spectroscopy (Figure 9.2c) confirm the purity of the resulting phase. Figure 9.2a shows the XPS survey spectrum obtained from surface of the nanorod arrays. Prominent peaks originating from zinc and oxygen are obvious. A small amount of carbon ($\approx 1\%$) is detected as
contaminant. Except for zinc, oxygen and carbon, no other elements were detected within the sensitivity of XPS. These results are consistent with EDX, where only zinc and oxygen can be detected (Figure 9.2b). The semiquantitative EDX analysis yields $\approx 55\%$ Zn and $\approx 45\%$ O.

Figure 9.2c shows the Raman spectrum of a ZnO nanorod array. The three main peaks are marked as A, B and C. The Raman peak at 334 cm$^{-1}$ (A) is originating from a multiphonon process$^{226,227}$, while the sharp peak at 437 cm$^{-1}$ (B) corresponds to the characteristic $E_2$ mode of ZnO with an hexagonal Wurtzite lattice$^{228,229}$. Additionally, a broad band detected around 578 cm$^{-1}$ (C), corresponds to LO phonons ($E_1$ and $A_1$ modes)$^{230}$. The observation of the LO phonon in the backscattering geometry used here is an indication of the presence of structural defects, see discussion elsewhere.$^{174,230,231}$

The effect of different electrolyte concentrations on the morphology of ZnO nanostructures was also investigated. In particular by exposing the zinc substrate to higher concentration of KCl (1 M and 3 M), the diameter of 1D ZnO nanostructure reduced from 70 nm to 10 nm. The resulting wire structures are not isolated, as in the case of lower electrolyte concentration. Instead of rods, which are observed for electrolyte concentrations below 1 M, pyramidal structures are formed, as shown in Figure 9.3a and b. An extreme case is observed when 3 M KCl is used, where thin ZnO nanorods are obtained (Figure 9.3c and 9.3d). The different diameters observed in electrolytes with different Cl$^-$ concentration are attributed to the modification of growth rates on different crystal faces by Cl$^-$ adsorption. As faces phases posses different polarities$^{192,232}$, different susceptibility towards ion adsorption is reasonable.

The observations made in this work indicate that the ZnO nanostructures grow after the passage of a delamination front under the polymer coating, as illustrated in Figure 9.4$^{12}$. The polymer itself has the function to contain a confined reaction environment, and is not actively participating in the reaction. In the cathodic initial region of the delamination front, oxygen reduction leads to the formation of alkaline conditions. After this part of the delamination front progressed through a certain region, the region becomes the local anode, where zinc dissolution to Zn$^{2+}$ occurs$^{12}$. Above a critical Zn$^{2+}$ concentration, when the pH is $>9^{233-235}$, zinc oxide nucleates. Due to the instability of one of the fundamental surfaces of ZnO, the oxide grows in rod-shape, as observed here$^{91,236}$. It is generally believed that low supersaturation levels favour 1D ZnO nanostructure growth$^{236}$. A schematic view of the process of cathodic delamination and consequent corrosion product growth is shown in Figure 9.4. In the absence of the polymer, i.e. when homogeneous corrosion of zinc occurs, no formation of rod-like nanostructures was observed. This cathodic delamination based nanorod synthesis approach is a sequential process, as opposed to the commonly practised synthesis approaches, in which nanorods grow in parallel over the full sample area$^{210,211}$.
Figure 9.1: (a) SEM image of ZnO nanorod array grown over a zinc substrate via tailored corrosion process carried out at room temperature, (b) magnified crossectional SEM image of ZnO nanorod arrays, (c) STEM micrograph of single nanorod, (d) HRTEM image with SAED pattern in the inset of single nanorods, (e) AFM topography image and (f) X-ray diffraction pattern.
9.2. Results

Figure 9.2: (a) XP survey spectrum, (b) EDX spectrum and (c) Raman spectrum of ZnO nanorod array.

9.2.2 Light absorption and photocatalytic activity

In general, electrochemically produced ZnO is known to have an electronic structure that is rather different from the electronic structure of bulk ZnO. In thin ZnO nanorods, quantum size effects may become important and defect levels lead to an absorption of light in the visible. Figure 9.5a shows the photoluminescence spectrum of the as-grown ZnO nanorod arrays measured at room temperature with excitation at 325 nm (3.81 eV). The nanorods exhibit a UV emission at ~368 nm (~3.4 eV), which corresponds to free excitonic emission, while wide visible emission band in the range of 500-700 nm (2.5-2 eV) is attributed to different structural defects in ZnO. Emission centred at 700 nm is generally attributed to oxygen interstitials. Emission
at lower wavelengths is attributed to oxygen vacancies\textsuperscript{230,238}. Because of the large peak width, a unique assignment of the spectrum to certain dominant defects is difficult, especially as other factors such as lattice strain cause energy shifts\textsuperscript{242}. A recent thermodynamic analysis of energy levels of point defects shows that ZnO is unstable towards Zn vacancy formation\textsuperscript{243}. Here, it is concluded that very likely a combination of several types of defects contribute to the observed luminescence. A UV/visible reflection absorbance spectrum of ZnO nanorods on the Zn substrate (Figure 9.5b) shows a strong increase in absorbance below 390 nm (3.2 eV), because of the main electronic transition in ZnO. However, in addition, a strong, structureless absorption of light is present throughout the visible spectral range, which is likely the result of a combination of multiple scattering of light in the nanorod arrays, and light absorption by the nanorods\textsuperscript{174}. The absorption is caused by defects in the ZnO crystal structure, while the rod-like morphology efficiently traps light via a multiple scattering process.

The absorption of visible light inspired the use of the ZnO structures in photocatalysis experiments using visible light. Previously, ZnO nanorods have been used
9.2. Results

Figure 9.4: Schematic representation of corrosion-driven growth of ZnO nanorods arrays.

as photocatalysts with excitation energies above the band gap e.g. for the degradation of pollutants or bacteria[244,245]. Here, the photocatalytic degradation of methyl orange (MO) under illumination with visible light was investigated. After starting red illumination, UV/visible spectra of the MO solution were measured (Figure 9.5c) and used to calculate the concentration of MO (Figure 9.5d). After 6 h of illumination at 633 nm, more than 90% of MO was decomposed. Two types of control experiments were conducted (Figure 9.5d). In the first control experiment, the solution was irradiated with the laser light in the absence of nanorod arrays and no decrease in MO concentration was observed (Figure 9.5d, green symbols). In the second control experiment, ZnO nanorod arrays were immersed in an MO aqueous solution, and the solution’s absorption spectra were recorded in the absence of illumination (Figure 9.5d, red symbols). In this case, a certain low decomposition was observed, but at significantly lower rate compared to the presence of illumination. If the light source at 633 nm is replaced by a light source at 532 nm, i.e. at a wavelength where the absorbance of MO is already significant, almost no decrease in MO concentration with time is observed. This observation is explained by the total absorption of light in the MO solution resulting in rather low intensity at the location of the ZnO nanorods. A presumable mechanism of the observed photocatalytic activity is the binding of diradical dioxygen to the exciton generated by light absorption, and a subsequent reaction of the generated oxygen species with the organic molecules. ZnO has been shown to facilitate the generation of reactive oxygen species[207,237]. “Free electron” defects inside the ZnO are also important for the catalytic activity in methanol synthesis[246]. While the TEM images and XRD patterns
confirm that crystalline ZnO is dominating in the produced nanorods, the presence of the visible photoluminescence,\textsuperscript{238} and the LO phonon in the Raman spectrum\textsuperscript{174}, point to a prominent presence of defects in the produced structures. Several types of defects are likely to contribute. Defect-related electronic states inside the band gap are responsible for the absorption of visible light. As the rod-like morphology leads to strong in-plane scattering of light, even low absorption coefficients will eventually lead to photon absorption after multiple scattering events. The observed photocatalytic activity is therefore a consequence of a combination of morphology and defect
structure in the ZnO.

9.3 Summary

In conclusion, a tailored corrosion process based on cathodic delamination of a polymer film on metallic zinc yields dense arrays of ZnO nanorods. This room-temperature process is extraordinarily simple. Because it relies on a sequential process, in this case the passage of a delamination front, the process can easily be upscaled to large areas. The resulting nanorod arrays have been shown to be able to use the red part of the visible spectrum to photocatalytically decompose methyl orange. The nanostructures produced by this method may potentially be used to decompose persistent pollutants. The wide availability of galvanised steel and the easy scalability of the process will enable a fabrication of the nanostructures on a m² scale. The nanorod synthesis scheme may also enable other (e.g. optoelectronic) applications of ZnO nanorods on large areas.
Chapter 10: Non destructive in situ Raman studies on the growth of ZnO nanorods

Introduction

In recent years, there has been a significant interest in synthesis of nanostructured materials owing to their unique and novel applications in catalysis, sensors, electronics, photonics, and mechanics. In particular, one dimensional (1D) ZnO nanostructures such as wires and rods have been extensively researched in the past few years due to their excellent optical, mechanical, and electrical properties. As 1D ZnO nanomaterials offer large surface area availability and quantum confinement effect, they exhibit a very fast response, high carrier mobility and novel properties which would improve the performance of future nanodevices. In order to produce high performance 1D ZnO based nanodevices, the synthesis of high quality ZnO nanorods is desired. Thus significant efforts have been devoted to the development of methods to synthesize high quality 1D ZnO nanostructures, such as chemical vapor deposition (CVD), vapor-liquid-solid growth (VLS), pulsed laser deposition, and hydrothermal approach. In recent times, hydrothermal approach has gained interest for the synthesis of 1D ZnO nanostructures due to their simplicity, commercial feasibility, and scalability. The pioneer work in this area has been carried out by Vayssieres et al., where they have synthesized ZnO nanorods on various heterogeneous substrates via solution phase approach. More recently, our group has further simplified this growth method by synthesizing ZnO nanorods via tailored corrosion process at room temperature.

Despite of significant progress in the synthesis of ZnO nanostructures, there are still some unanswered questions concerning the performance and reliability of ZnO based devices. For instance, for all synthesized ZnO nanostructures, there is a trade-off between conductivity and near band edge emission (NBE) efficiency. High conductivity in ZnO is achieved by increasing the number of defects in a ZnO crystal structure that provides sufficient free carriers. However, this comes with a compromise in NBE emission efficiency due to direct interband radiative recombination. Moreover, application of ZnO nanomaterials in a visible light photocatalysis is strongly dependent on the concentration of oxygen deficiencies.
or other native defects in a crystal structure, which is responsible for visible light absorption in ZnO. Hence, one of the factors which play a vital role in achieving the desired property of ZnO based nanodevice is the optimal concentration of defects in a nanomaterial. A key towards resolving these issues lies in the detailed understanding of ZnO nanostructure growth process. Most of the previous studies performed to probe the growth kinetics of ZnO nanostructures are achieved by using the UV-Vis spectroscopy\textsuperscript{258,259}. More recently, laser assisted hydrothermal growth of ZnO nanowires was investigated based on optical in situ growth monitoring\textsuperscript{260}. However, both of the above mentioned strategies only gives insight into the growth of crystals and no information on the evolution of crystal/electronic structure of ZnO could be obtained. Indeed, properties of ZnO nanostructures depend not only on their size but also on the crystal structure. Hence, it is also vital to study the evolution of crystal structure during the growth of ZnO nanostructure. X-ray diffraction is a widely used technique to probe the crystal structure of nanomaterials; however it is evidently quite difficult to use it for in situ measurement during the hydrothermal growth. Hence, another fast and non-destructive technique is required for in situ monitoring of crystal structure and growth kinetics of ZnO.

Raman spectroscopy is a well-established nondestructive technique to study the chemical composition, crystal structure and defects in a nanomaterial. It has been widely used to probe the physical state, phonon confinement, and crystal structure of ZnO\textsuperscript{135}. ZnO belongs to the P6\textsubscript{3}mc space group, where all atoms occupy C\textsubscript{3v} sites. According to group theory, four Raman active modes of A\textsubscript{1}, E\textsubscript{1}, and E\textsubscript{2} (high and low) are expected for wurtzite ZnO. The phonons belonging to A\textsubscript{1} and E\textsubscript{1} symmetry are polar and therefore exhibit different transverse-optical (TO) and longitudinal-optical (LO) frequencies\textsuperscript{261}. On the other hand, E\textsubscript{2} modes are due to the vibration of Zn sub-lattice (E\textsubscript{2}-low) or O sublattice (E\textsubscript{2}-high). With the Raman active modes of ZnO, recently Raman spectroscopy is utilized to determine the crystal orientation of anisotropic ZnO nanorods\textsuperscript{252}. Moreover, it has been employed for in situ analysis of electronic and structural aspects of passive ZnO film grown under alkaline conditions\textsuperscript{262}. This provides us the motivational grounds to utilize Raman spectroscopy for in situ studies on growth kinetics of ZnO nanorods.

In this chapter, kinetic studies on the growth of ZnO nanorods synthesized via a tailored corrosion process by performing in situ Raman experiments has been carried out. Furthermore, the effect of salt concentration on the growth and crystal structure of ZnO nanorods was also studied.

### 10.1 Experimental details

#### 10.1.1 Materials

Polyvinyl butyral (PVB), absolute ethanol and KCl were obtained from Sigma Aldrich and used as received. Zinc sheets (purity, 99.95\%) having a thickness of 1.5 mm were obtained from Goodfellow (Cambridge, UK). Zinc sheets were initially
mechanically polished using 4000 grit polishing paper and then cleaned ultrasonically in ethanol.

10.1.2 Synthesis of ZnO nanostructures

Initially polished zinc sheets (1 cm × 1 cm × 1.5 mm) were spin coated with 5 wt% solution of PVB in ethanol followed by drying in an oven at 70 °C, to obtain 2 µm thick polymer layer. Afterwards, small defect in the polymer coating was created at the edge of the sample and the sample was placed on zinc base plate. Then small reservoir was built around the edge of the sample with the help of fast drying two components adhesive to place an electrolyte. To start the growth of ZnO nanowires via tailored corrosion process, reservoir was filled with 1 M aqueous KCl solution (unless noted otherwise). After completion ZnO nanowires growth, PVB coating was removed by washing with ethanol, followed by rinsing with distilled water to remove any traces of remaining KCl. The washed samples were dried in nitrogen stream and stored in vacuum for further analysis.

10.1.3 Analytical techniques

The surface morphology ZnO nanowires were obtained by Scanning Electron Microscopy (SEM, Zeiss/LEO 1550 VP). Before introducing the samples into SEM chamber, PVB coating was removed by excess cleaning with ethanol in order to avoid sample charging. Crystallographic information about the nanorods was obtained by X-ray diffraction (XRD, Bruker-AXS D8 with a Cu-Kα source) in grazing incidence geometry.

To carry out in situ Raman measurements, the assembly of sample mounted on zinc substrate was introduced into a custom made chamber with a glass window opening to allow spectral acquisition. To minimize electrolyte evaporation, the humidity was controlled ≥90% with the help of humid/dry air flow. The in situ Raman spectra’s were recorded using a Horiba Jobin Yvon LabRAM confocal Raman microscope with a Argon laser source (emission wavelength is 514.342 nm) and a power of 12 mW. The typical spectral acquisition time was in the range of 20 to 30 s. The measurements were performed in reflection geometry with a 50x-objective for sample illumination and scattered light harvesting. The laser spot size on the sample surface was approximately 1 µm.

10.2 Results and discussion

Prior to the growth of nanorods, zinc substrate was spin coated with 5 wt% PVB in order to have a thin layer of polymer covering the whole surface. The presence of thin polymer layer hinders the immediate spreading of an electrolyte over the whole sample surface and only allows an ultra-thin layer of an electrolyte to go through polymer/metal interface. The sample was then introduced into a custom made
Chapter 10. In situ Raman studies on the growth of ZnO nanorods

chamber, where the humidity was controlled above 90% via flow of humid/dry air. Later on, the coated zinc was exposed to 1 M KCl in order to grow ZnO nanorods via cathodic delamination process. The detailed mechanism of ZnO nanorods growth via cathodic delamination is explained in chapter 8. The setup for in situ measurements is shown schematically in Figure 10.1.

![Schematic representation of experimental setup for in situ Raman measurements of ZnO nanorods growth via cathodic delamination.](image)

Figure 10.1: Schematic representation of experimental setup for in situ Raman measurements of ZnO nanorods growth via cathodic delamination.

The growth kinetics was monitored at a measurement spot via in situ Raman experiment. Figure 10.2 shows the measured Raman spectra over a corroding sample as a function of time. At the initial stages of experiment, hardly any discernible peaks could be observed for freshly polished and polymer coated zinc substrate. However, as the electrolyte/delamination front approaches the measurement spot, the band at 565 cm$^{-1}$ begins to evolve (see Figure 10.2a). This peak is attributed to A$_1$-LO phonon mode of ZnO, indicating the growth of amorphous ZnO$^{228}$. This growth is caused by degradation of bonds at metal/polymer interface which induces local pH
changes in the vicinity of delamination front by oxygen reduction (pH increase) or by formation of zinc-hydroxide complexes (pH decrease). Zn(OH)$_2$ is believed to be a precursor that forms during corrosion of zinc and which eventually precipitates as the solution becomes supersaturated to form ZnO. However, no evidence for the presence of Zn(OH)$_2$ within the sensitivity level of these in situ Raman measurements could be found. This is in agreement with the previous studies performed on zinc under alkaline conditions$^{262}$. As the time progresses, one additional band evolve at 438 cm$^{-1}$ and starts to grow. This peak is assigned to E$_2$-high phonon mode of ZnO, indicating the growth of wurtzite ZnO crystals$^{228}$. After 12 h, no further increase in the peak intensity has been observed, which indicates that the growth of crystalline ZnO is no more pronounced. The increase in a peak height of wurtzite ZnO (438 cm$^{-1}$) and amorphous ZnO (565 cm$^{-1}$) as a function of time is depicted in Figure 10.2b. The plot clearly demonstrates the monotonic increase in the peak intensities ratio over time. The possible explanation of this phenomenon

Figure 10.2: In situ monitoring of ZnO nanorods growth via tailored corrosion process with 1 M KCl. (a) In situ Raman spectra acquired during growth of ZnO nanorods as a function of time, (b) intensity ratios of wurtzite ZnO and defect rich ZnO peaks with respect to the baseline, (c) intensity ratio of wurtzite ZnO peak vs amorphous ZnO peak.
is the depletion in the concentration of Zn(OH)$_2$ or neutralization of the interfacial pH, which is responsible for the growth of ZnO by dehydration. As ZnO grows on zinc, the rate of zinc oxidation goes down due to passivation of the surface. This also leads to decrease in the rate of O$_2$ reduction (as it has to diffuse through the formed passive film) which is responsible for the formation of OH$^-$ ions. Hence, the interfacial pH value gets lower, which prevents any further precipitation of ZnO.

To gain insight into the competing behavior of two growing peaks, the height ratio of wurtzite ZnO peak (440 cm$^{-1}$) versus amorphous/defect rich ZnO peak (565 cm$^{-1}$) as a function of time (see Figure 10.2c) is plotted. It can be seen that at initial stages of growth, peak height ratio results in a value lower than 1, indicating growth of defect rich ZnO. However, after the initial period of the experiment (after ca. 2 h), growth of wurtzite ZnO becomes dominant as can be seen in Figure 10.2c. Finally after approximately 12 h the ratio becomes stable, indicating that no further changes in the crystal structure of growing ZnO takes place. This leads to conclude that initially, growth of amorphous ZnO is favored, while in the later stages more crystalline ZnO nanorods grow.

Figure 10.3 shows the Raman and PL spectra performed along the length of the nanorod cluster using 514 nm and 355 nm excitation wavelength, respectively. For better visualization of differences in the peak intensities along the length of the rod, different colors are used in a spectra. Figure 10.3I shows the room temperature PL mapping performed (using 355 nm excitation wavelength) along the length of the nanorod cluster. The spectrum is marked with A, B and C corresponding to the lower region, middle region and upper region of the nanorod, respectively. It is quite evident that the intensity of green emission which is related to the presence of oxygen vacancies (or other point defects)$^{238}$ is different along the length of the nanorod cluster. On one hand, the PL intensity of green emission is lower for upper region (C) of ZnO nanorods, indicating that the ZnO nanorod cluster has a low defect density$^{263}$ and good crystallinity$^{264}$. While on the other hand, higher green emission intensity at the bottom of the rod represents the higher density of oxygen-related defects. On the same nanorod cluster, Raman mapping was performed along the length using 532 nm excitation source. The change in the intensity could be identified for two main bands centered at around 438 cm$^{-1}$ (E$_2$-high) and 565 cm$^{-1}$ (E$_1$-LO) (see Figure 10.3II). Initially, at the lower end of the nanorod cluster (marked with A), the intensity of E$_1$ band is higher indicating the presence greater amount of defects, while in the upper region (marked with C) the intensity of E1 band gets lower indicating presence of more crystalline ZnO. The region marked with B indicates the presence of both crystalline and defect rich ZnO. Hence, ex situ Raman analysis performed along the length of nanorod cluster, further confirms the statement that at the initial stages, ZnO nanorod has a defect rich structure which eventually gets more crystalline as the growth proceeds.
10.2. Results and discussion

Figure 10.3: Raman mapping of ZnO nanorod arrays. (I) PL spectra along the length of the nanorod array with 355 nm excitation wavelength, (II) Raman spectra along the length of the nanorod array with excitation wavelength of 514.32 nm, (III) SEM image of a nanorod cluster used in ex-situ experiments.

10.2.1 Change in surface morphology during growth

To gain further insight into the changes in the morphology of growing ZnO nanorods, SEM micrographs with their corresponding Raman spectra were obtained after specific time intervals (see Figure 10.4). As shown in Figure 10.4-Ia, the zinc surface is covered with the thin oxide layer during the initial stages of growth. This grown oxide is amorphous which is evident from the attributed Raman spectra (Figure 10.4-Ic) where only the peak at 568 cm$^{-1}$ is present that corresponds to the defect rich/amorphous ZnO. After approximately an hour, nanorod type structure of ZnO starts to grow as can be seen in Figure 10.4II, which can be confirmed by appearance of 440 cm$^{-1}$ peak in the acquired Raman spectra. Finally after 12 h, the ZnO nanorods are grown upto 1 µm (see 10.4-III) and the wurtzite ZnO peak is dominant.
Figure 10.4: SEM micrographs with their corresponding Raman spectra. (I) after 15 mins, (II) after 1 h, (III) after 12 h. (a) top view, (b) cross-sectional view (c) ex situ Raman spectra.

in the corresponding Raman spectra. The comparison of the relative height of two bands at 440 cm$^{-1}$ and 568 cm$^{-1}$ suggests that the band at 440 cm$^{-1}$ increases more intensively with time than the band at 568 cm$^{-1}$. This observation also suggests that the concentration of defects in a growing ZnO crystal reduces as the growth progresses.

### 10.2.2 Effect of electrolyte concentration

Previous studies have shown that corrosion of zinc is accelerated by increase in the concentration of Cl$^{-}$ ions in aqueous solutions$^{265,266}$. Hence, it is important to study the effect of chloride concentration on the growth kinetics of ZnO nanorods. Consequently, PVB coated zinc surface was exposed to 3 M KCl in a humid air atmosphere and the growth kinetics was monitored via in situ Raman experiments. Figure 10.5a depicts the measured Raman spectra over a corroding zinc sample as a function of time. As in the case of 1 M KCl, initially the peak at 566 cm$^{-1}$ appears which corresponds to growth of defect rich ZnO. Later on, wurtzite ZnO
10.2. Results and discussion

peak evolves at $440 \text{ cm}^{-1}$ and grows over increasing period of time. However, increase in the intensity of wurtzite ZnO band stops approximately after approximately 4 h. This suggests that no further growth or modification of ZnO takes place. To track the changes in the crystal structure, the height ratio of wurtzite ZnO peak and defect rich ZnO peak is plotted as performed in the case of 1 M KCl. As shown in 10.5c, for approximately initial 30 minutes the ratio stays below 1, which is an indication that growth of defect rich ZnO is more pronounced then growth of wurtzite ZnO. It is also interesting to see a sharp dip in a curve after nearly 15 min, which shows an increased rate in the growth of defect rich ZnO. Afterwards, the ratio goes over 1, indicating that now wurtzite ZnO crystal structure is growing more intensively. Finally, the ratio becomes stable after approximately 4 h which indicates that there are no more changes in the crystal structure taking place. The result depicts a similar trend for growth of ZnO nanorods in both 1 M KCl and 3 M KCl except the growth rate is increased in the latter case. This increased rate in growth of ZnO nanorods is caused by fast zinc corrosion due to higher electrolyte concentration. Moreover, slightly higher ratio of amorphous/defect rich ZnO peak suggest the presence of higher number of oxygen deficiencies in ZnO nanorods grown with 3 M KCl in comparison with rods grown with 1 M KCl.

10.2.3 Optical properties of ZnO nanorods

As known from the literature, the optical properties of ZnO nanostructures such as photoluminescence and visible light absorption strongly depends on the presence of defects that are present in the crystal of an oxide. Indeed, in situ Raman measurements showed above reveals the presence of higher number of oxygen deficiencies (or point defects) evident from the higher oxygen deficient peak intensity (see Figure 10.5) in a nanostructure grown with 3 M KCl. Hence, to verify this statement, UV/Vis absorption spectra (in reflection geometry) of as grown ZnO nanostructures with 1 M and 3 M KCl were measured and are shown in 10.7. The spectra show a strong absorption at around 372 nm, which corresponds to the charge-transfer process from valance band to conduction band. However, the light absorption in the visible range is higher for wires synthesized with 3 M KCl then for 1 M KCl. This could be explained by the fact that the higher concentration of oxygen defects (or point defects) in nanorods grown with 3 M KCl leads to increased absorption in the visible light region.
Chapter 10. In situ Raman studies on the growth of ZnO nanorods

Figure 10.5: In situ monitoring of ZnO nanorods growth via tailored corrosion process with 3 M KCl. (a) In situ Raman spectra acquired during growth of ZnO nanorods as a function of time, (b) Intensity ratios of wurtzite ZnO and defect rich ZnO peaks with respect to the baseline, (c) intensity ratio of wurtzite ZnO peak vs amorphous ZnO peak.
10.2. Results and discussion

Figure 10.6: SEM micrographs and their corresponding Raman spectra measured ex situ after different delamination times. (I) after 15 min, (II) after 4 h, (a) top view, (b) cross-sectional view (c) corresponding ex situ Raman spectra.
10.3 Summary

In situ Raman studies of ZnO nanorod growth reveals that at the initial stages of growth, nucleation of defect rich ZnO takes place, while in the later stages growth of wurtzite ZnO becomes pronounced. The growth of nanorods stops due to depletion in the concentration of zinc hydroxide complexes which is responsible for the growth of ZnO via dehydration. Moreover, it was also shown that the nanorod growth kinetics could be accelerated by increasing the concentration of an electrolyte. These results provide a key insight into the growth kinetics and evolution of the crystal structure of ZnO nanorods which could play a vital role in their future optoelectronic applications.
Chapter 11: Summary and Outlook

11.1 Summary

Ultrathin polymer coatings were synthesized by thermally initiated free radical polymerization on top of zinc substrates. These coatings were covalently bound to the surface with well defined interfacial chemistry. In order to alter the adhesion properties, polymer coatings were grown on top of silane and ester functionalized zinc samples. Moreover, PMMA and PS were employed as a model polymers to study the cathodic delamination behavior as they mimic the properties of both aliphatic and aromatic based polymers used as polymer coatings in corrosion protection. In order to alter the polymer structure, PMMA and PS coatings were crosslinked by adding bifunctional molecule having different aliphatic chain length (ethylene diacrylate, EDA and hexanediol diacrylate, HDA) and were added in different molar ratios (i.e. 25 mol% and 50 mol%). The thickness of the model polymer coatings were in the range of 10-25 nm.

Scanning Kelvin probe measurements shows that chemisorbed polymer coatings show larger resistance against cathodic delamination than physisorbed PVB coating. The delamination rate decreases to $<1/10$ only by introducing covalent bonds to the base metal. Moreover, it was also shown that silane bonded PMMA coatings exhibit larger resistance against cathodic delamination than coatings attached to the substrate via ester bond. This enhanced resistance is a result of strong silane bond at the polymer/metal interface. While for ester bound PMMA coating, the bond at polymer/metal interface is relatively weak and susceptible to alkaline ester hydrolysis. Introduction of a cross-linker to a silane and ester bonded PMMA coating further slows down the delamination rate, with another factor of $\sim 10$ between non-cross-linked PMMA and samples with 50% cross-linker. Comparing the two cross-linkers used in this study, the more hydrophobic HDA yields the lowest delamination rates of all samples.

Similarly, PS coatings bound to zinc via organosilanes show enhanced resistance against cathodic delamination when compared with coating bound exclusively via van der Waals interactions. Furthermore, PS coating without cross-linker shows larger resistance toward cathodic delamination when compared to linear PMMA coatings. This enhanced resistance is attributed to higher hydrophobicity of PS. However, adding a cross-linker to PS coatings does not significantly reduces the delamination rate.
Chapter 11. Summary and Outlook

The cathodic delamination rates of PMMA coatings synthesized in this work on metal substrates are not diffusion limited but are reaction controlled. On the other hand, for PS coatings, initially the cathodic delamination is reaction controlled but becomes diffusion controlled after long times.

For a study of the dependence of cathodic delamination on interface morphology, different ZnO structures (i.e. twin-plate, nanorod, and sphere) were synthesized. PVB was used as a model coating to exclude the covalent interaction at polymer/oxide/metal interface. The delamination was fastest for twin-plate-shaped particles, and lowest for spherical ZnO particles. Moreover, the comparison of the surface morphologies before and after the delamination experiments shows that dissolution of the oxide in the interfacial region occurs. The kinetics of delamination is likely determined by the nature of the dominating surface termination of ZnO. These results suggest that controlling the oxide surface morphology offers the chance to significantly increase resistance of polymer-coated galvanized steel towards cathodic delamination.

After evaluating the effect of different ZnO morphologies on the cathodic delamination kinetics, it was of interest to study the corrosion products formed at the surface as a result of zinc corrosion. Hence, corroded zinc substrates were characterized by SEM to analyze the corrosion products formed at the surface. The results revealed the formation of ZnO nanorod structures at the surface. This provides a unique and tailored corrosion process based on cathodic delamination of a polymer film to yield dense arrays of ZnO nanorods. This synthesis route is extraordinarily simple and carried out at room temperature, hence can easily be up-scaled to large scales. Moreover, the resulting nanorod arrays have been shown to be able to use the red part of the visible spectrum to photocatalytically decompose methyl orange.

The investigation of growth of ZnO nanorods with in situ Raman experiments were performed with the aim to investigate and get further insights into the growth mechanism via the tailored corrosion process. The results show that the defect concentration was different along the length of the nanorods. In particular, at initial stages of growth, nucleation of defect rich ZnO takes place, while in the later stages growth of wurtzite ZnO becomes pronounced. Moreover, it was also shown that defect concentration in ZnO nanorods could be altered by varying the concentration of electrolyte used for the cathodic delamination process.

The results presented in this work may contribute to the fundamental understanding of interactions at polymer/metal interface. In particular the disbonding kinetics of polymer coatings from metal substrates due to cathodic delamination. It further allows to utilize the mostly undesired cathodic delamination process to synthesize ZnO nanorods at large scales via a very simple and economically feasible process. Moreover, the application of these as synthesized ZnO nanorods in visible light photocatalytic decomposition of methyl orange provides a potential way to be used to decompose persistent pollutants.
11.2 Outlook

Based on the fundamental and technical understanding achieved in this work, a solid basis for further investigations and step out to industrial applications can be proposed. Consequently, it would be valuable to study the delamination kinetics of polymer coatings bonded to metal substrate via different covalent bonds such as ether and amide linkages. Both amide and ether linkages have already been shown to bound to inorganic substrates via covalent bonds\textsuperscript{30}. Furthermore, in order to achieve polymer coatings with well defined chain lengths, it is also desirable to utilize controlled radical polymerization approaches such as atom transfer free radical polymerization. Comparing the delamination kinetics of these differently bonded polymer coatings to the metal substrates could provide the basis for the improvements in the commercially applied polymer coatings for corrosion protection. Furthermore, the tailored corrosion route developed in this work for the fabrication of ZnO nanorods on metallic zinc at room temperature could be used to grow ZnO nanostructures on other inorganic substrates. In particular, for optoelectronic applications such as solar cells, ZnO nanorods grown on surfaces like silicon and/or polymers are of high technological interest. However, due to complexities in the growth process of ZnO nanostructures, their fabrication on top of these inorganic substrates is limited. The proposed route in this work for fabrication of ZnO nanorods provides mild growth conditions that could be used grow ZnO nanostructures on top of substrates interesting for optoelectronic applications.
Bibliography


# List of Figures

1.1 Schematic representation of steps in classical free radical polymerization 3
1.2 Schematic representation of covalent modification of oxide surfaces 5
1.3 Schematic representation of cathodic delamination of polymer coated zinc substrate 7
1.4 Potential-pH equilibrium diagram (pourbaix) for zinc 11

2.1 Schematic representing the route to delamination studies 16
2.2 Schematic representation of functionalization of zinc 18
2.3 Schematic representation of synthesis of PMMA and PS polymers 19
2.4 Layout of flow chart depicting the schematic of thesis chapters 21

3.1 Schematic representation of in situ photocatalysis experiment 32

4.1 Scheme of the surface modification steps carried out in this chapter 36
4.2 IR and XP spectra of VTS modified zinc 37
4.3 TOF-SIMS spectra of VTS modified zinc 38
4.4 XPS survey spectrum on chemisorbed PMMA coating 38
4.5 IR and C 1s XP spectra of silane bound PMMA coating 39
4.6 SKP delamination profile of silane bound PMMA and physisorbed PVB coated zinc 41
4.7 Comparison of the delamination rates for silane bound PMMA coatings 42
4.8 Tafel plots for silane bound PMMA coatings 44
4.9 Bode plots of silane bound PMMA coatings 45

5.1 Synthetic route for the synthesis of silane bonded PS coatings 50
5.2 IR spectra silane bound PS coatings 51
5.3 C 1s region of the XP spectra of PS modified zinc 52
5.4 SKP delamination profile of silane bound PS and physisorbed PVB coating 54
5.5 Comparison of the delamination rate of PS modified zinc 55

6.1 Scheme of the surface modification steps carried out in this chapter 58
6.2 (I) IR and (II) C 1s XP spectra of ester modified zinc 59
6.3 TOF-SIMS spectrum of acryloyl chloride modified zinc 60
6.4 (I)IR and (II) C 1s XP spectra of ester bound PMMA coatings 61
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>SKP delamination profile of ester bound PMMA and physisorbed PVB coating</td>
<td>63</td>
</tr>
<tr>
<td>6.6</td>
<td>Comparison of the delamination rate for ester bound PMMA coatings</td>
<td>64</td>
</tr>
<tr>
<td>7.1</td>
<td>Comparison of delamination rates of chemisorbed linear PS and PMMA polymer coatings</td>
<td>66</td>
</tr>
<tr>
<td>7.2</td>
<td>Comparison of delamination rates of chemisorbed 50% EDA cross-linked PS and PMMA polymer coatings</td>
<td>67</td>
</tr>
<tr>
<td>8.1</td>
<td>SEM micrograph and XRD pattern of grown ZnO structures on zinc</td>
<td>71</td>
</tr>
<tr>
<td>8.2</td>
<td>SKP delamination profiles of zinc with and without ZnO nanostructures</td>
<td>72</td>
</tr>
<tr>
<td>8.3</td>
<td>Comparison of delamination rates</td>
<td>73</td>
</tr>
<tr>
<td>8.4</td>
<td>SEM micrographs after the delamination</td>
<td>74</td>
</tr>
<tr>
<td>9.1</td>
<td>SEM image of ZnO nanorod arrays</td>
<td>80</td>
</tr>
<tr>
<td>9.2</td>
<td>XPS, EDX and Raman spectra of ZnO nanorod arrays</td>
<td>81</td>
</tr>
<tr>
<td>9.3</td>
<td>SEM micrograph of ZnO nanorod grown with different electrolyte concentration</td>
<td>82</td>
</tr>
<tr>
<td>9.4</td>
<td>Schematic representation of corrosion-driven growth of ZnO nanorods arrays</td>
<td>83</td>
</tr>
<tr>
<td>9.5</td>
<td>(a) PL spectrum of ZnO nanorod arrays, (b) reflection absorption spectrum of ZnO nanorod arrays, (c) UV/visible spectrum of MO solution after different irradiation times, (d) molar concentration of MO as function of time under illumination</td>
<td>84</td>
</tr>
<tr>
<td>10.1</td>
<td>Experimental setup for in situ Raman measurement of ZnO nanorods</td>
<td>90</td>
</tr>
<tr>
<td>10.2</td>
<td>In situ monitoring of ZnO nanorods growth with 1 M KCl</td>
<td>91</td>
</tr>
<tr>
<td>10.3</td>
<td>Raman mapping of ZnO nanorod cluster</td>
<td>93</td>
</tr>
<tr>
<td>10.4</td>
<td>SEM micrographs with their corresponding Raman spectra</td>
<td>94</td>
</tr>
<tr>
<td>10.5</td>
<td>In situ monitoring of ZnO nanorods growth with 3 M KCl</td>
<td>96</td>
</tr>
<tr>
<td>10.6</td>
<td>SEM micrographs and their corresponding Raman spectra measured ex situ after different delamination times</td>
<td>97</td>
</tr>
<tr>
<td>10.7</td>
<td>UV/VIS reflection absorption spectrum of ZnO nanorod arrays</td>
<td>98</td>
</tr>
</tbody>
</table>
## List of Tables

4.1 Thickness of silane bound PMMA coatings ........................................... 40
4.2 Delamination rates and standard deviations of silane bound PMMA coatings ................................................................. 43
4.3 Corrosion current densities of silane bound PMMA coatings ............... 44
5.1 IR stretching vibration position of PS coatings ................................. 51
5.2 Thickness of PS coatings ................................................................. 53
5.3 Comparison of delamination rate of PS coatings ............................... 55
6.1 IR stretching vibration position of PMMA coatings ............................ 62
6.2 Thickness of ester bound PMMA coatings ......................................... 62
6.3 Delamination rate and standard deviation of ester bound PMMA coatings ................................................................. 63
7.1 Delamination rates and standard deviations for the different samples ... 68
### 3 Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<td>AIBN</td>
<td>Azobisisobutyronitrile</td>
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<td>PVB</td>
<td>poly(vinyl butyral)</td>
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<td>EDA</td>
<td>Ethylene glycol diacrylate</td>
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<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
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<td>hexamethylenetetramine</td>
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<td>IR</td>
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<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<td>Methyl orange</td>
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<td>PS</td>
<td>Poly(styrene)</td>
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<td>SEM</td>
<td>Scanning electron microscope</td>
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<td>SKP</td>
<td>Scanning Kelvin probe</td>
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<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
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<td>THF</td>
<td>Tetrahydrofuran</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
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Training Production module of SAP (Enterprise Software)