



Study of the buried interface between zinc and emeraldine base coating



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ABSTRACT

The corrosion protection mechanism by polyaniline based coatings on metals is widely suggested to be due to the formation of an improved interfacial passive layer. However, it is argued against this that just an improved passive layer is not sufficient on metals such as iron and zinc for providing significant delay of cathodic delamination. Instead a significant inhibition of oxygen reduction is required, e.g. by an electronically insulating oxide. In this work results are presented providing proof for the formation of a highly electronically insulating and stable zinc oxide layer underneath an emeraldine base composite coating. It is shown how the Scanning Kelvin Probe (SKP) can be used to screen for such highly insulating oxide layers underneath coatings containing conducting polymer.

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1. Introduction

Over the last 30 years application of polyaniline (PANI) for corrosion protection of various metals has drawn great attention in academia and in industry [1]. Since DeBerry [2] claimed a highly efficient protection performance of PANI on steel in 1985, it has been an attractive candidate for the further research on corrosion protection. One of the most extensively proposed protection mechanisms suggested in a vast number of publications on the corrosion protection by conducting polymer is the formation of a protective oxide layer at the metal/coating interface [3–8], which is induced by PANI as oxidizer.

However, it should be mentioned that although the vast majority of publications on the use of conducting polymers for corrosion protection report very positive results, this is in fact not generally accepted, see e.g. Gustavsson et al. [9] and especially Michalik et al. [10]. In the latter work, one conclusion is that contiguous conducting polymer coatings should not be used (e.g. electrodeposited conducting polymer coatings). Instead composite coatings of a non-conducting matrix containing conducting polymer additions are recommended. Excellent critical overviews of the latest status quo on conducting polymers for corrosion protection can be found in the reviews by Rohwerder [11] and Gelling [12].

Concerning the role of an improved passive layer, although most authors claim that the passivation of the metal surface by conducting polymers plays a role, in the work by Holness et al. [13], it was convincingly demonstrated that the thicker oxide layers induced by PANI emeraldine salt (ES) e.g. on iron did not much affect the corrosion behaviour. It was also shown by the same group that significant oxide layer growth could occur, an indication, in fact, for enhanced corrosion underneath the ES [14].

For the case of ES on zinc, however, no enhanced corrosion was found. On the contrary, the formation of a highly insulating and obviously also very protective interfacial layer has been proposed [15]. This is based on the observation that although PANI as well as polypyrrole on top of zinc is not reduced, the potential measured by Kelvin probe on ES or polypyrrole applied on zinc is very low, several hundreds of mV lower than the potential of corresponding to ES or polypyrrole [14–16]. Williams et al. [14] proposed that for the case of ES this was due to a deactivation of ES owing to the basic nature of the interfacial zinc (hydr) oxide formed between coating and substrate, which eventually leads to the conversion of ES into EB. As a consequence an insulating layer was formed at the interface. Michalik et al. [15] reported that the interfacial layer was indeed highly insulating and that might in fact result in a very good corrosion protection [11]. The findings of Meroufel et al. [17], concerning the good performance of ES-modified zinc rich primers, could be possibly explained by this interfacial layer, and maybe also the decreased delamination of ES/PVB on zinc observed by Williams et al. [16].

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Concerning PANI emeraldine base (EB) for the corrosion protection of zinc the published literature is more contradictory than for ES. Williams et al. [18] reported that there were no positive effects observable for EB on zinc and also no ennoblement was seen. Furthermore, even for EB coated iron and aluminium no ennoblement was observed, while it occurred for ES [14]. As already mentioned above, on zinc, however, also ES shows no ennoblement, although a significant decrease of cathodic delamination was observed [18]. As discussed above, the missing ennoblement for the case of ES on zinc is due to the formation of an insulating layer at the interface between metal and ES, which is suggested to be also the reason for the decrease in delamination rate of organic coatings containing ES. It seems likely that for EB this is also the case, causing Fermi level misalignment and hence only apparently low potentials. If this is true, also some positive effect should be observable for EB on zinc. Indeed, there are reports about improved corrosion protection of EB on steel [4,19], aluminium alloy [20], and magnesium alloy [21].

In this work we will show that indeed also the zinc oxide beneath EB composite coating is changed and shows by itself an extremely protective behaviour against further oxidation. The main techniques applied for this study are X-ray photoelectron spectroscopy (XPS) and Scanning Kelvin Probe (SKP), which can detect the work function changes caused by electrochemical reactions beneath organic coatings [15], but also provides crucial information of chemical and/or physical changes in the oxide layer formed on the metal surface [22–24].

2. Experimental

Iron and zinc sheets of 1.5 mm thickness (99.99%) were purchased from Goodfellow and cut to specimens with a dimension of 20×20 mm. They were ground with SiC paper (up to 1000 grit), cleaned with water and ethanol, and dried with a N_2 stream. Polyvinyl butyral (PVB, $M_w \approx 50,000$ – $80,000 \text{ g mol}^{-1}$) were purchased from Sigma–Aldrich, and EB powder ($M_w \approx 22,000 \text{ g mol}^{-1}$ with polydispersity index of 3.7) was obtained from Ben'an Co., China.

EB/PVB composite coatings were prepared by admixing calculated amount of EB powder and PVB solution (14 wt. %) in ethanol. Then the EB/PVB dispersions of $10 \mu\text{L}$ were drop coated on a part of metal surface and dried at 75°C . Four different coatings were obtained by adjusting the volume fraction of EB in PVB matrix: pure PVB coating without EB pigment, and EB/PVB coatings containing EB of 7 vol. %, 15 vol. % and 30 vol. %, labelled as PVB, 7%

EB/PVB, 15%EB/PVB and 30%EB/PVB, respectively. The volume fraction was calculated by using densities of 0.8 g cm^{-2} and 1.25 g cm^{-2} for PVB and EB, respectively. The thickness of coating was around $30 \mu\text{m}$.

To investigate the interfacial reactivity between coating and metal substrate, the potential profiles starting from the center of coating towards the uncoated part of metal were monitored by line scanning of SKP under wet air (90% r.h., at room temperature) and then wet nitrogen (90% r.h., at room temperature). After the experiment, coatings were removed in ethanol via ultrasonic bath. For half tested samples, the buried surfaces were subsequently characterized by XPS. The other half were monitored by SKP in wet nitrogen for further 3 hours (90% r.h.) to obtain the potential profiles starting from the center of the previously buried interface to the previously uncoated Zn, and then XPS was carried out on the buried interfaces. XPS measurements were performed with a PHI Quantera II (Physical Electronics, Chanhassen, MN, USA) using a monochromatic Al K (alpha) radiation source (1486.7 eV) operating at 15 kV and 25 W. For XPS sputtering, the underlying zinc surface was bombarded with Ar^+ ions for 1 minute at a sputter rate of 2.54 nm min^{-1} .

3. Results and discussion

For the investigation of the interfacial reactivity a similar procedure as described in an earlier work [25] was applied. First, all coated samples are measured in humid air (90% r.h.), where moisture will be up-taken by the coating. When the water penetrates to the coating/metal interface this may lead to an interfacial corrosion reaction, depending on whether the metal surface is passive or not. In the second step, the atmosphere in the SKP chamber is changed to humid nitrogen (90% r.h.). Under this circumstance, due to the absence of the oxidizing power of oxygen the potential on reactive surfaces decreases [25]. If no change can be seen this indicates electrochemically inactive surfaces and/or interfaces [25].

PANI-EB is in the same oxidation state as PANI-ES, but non-conductive, or rather much less conductive than ES, which should decrease its electrochemical activity. Nevertheless, the work function of EB should correspond with its oxidized state, i.e. comparable values as for ES should be acquirable. Fig. 1 shows Kelvin probe measurements performed on two iron samples partly coated with PVB coating and 30%EB/PVB composite coating, respectively. As can be seen a potential of about $400 \text{ mV}_{\text{SHE}}$ is measured on the EB/PVB coated iron area, while the potential is

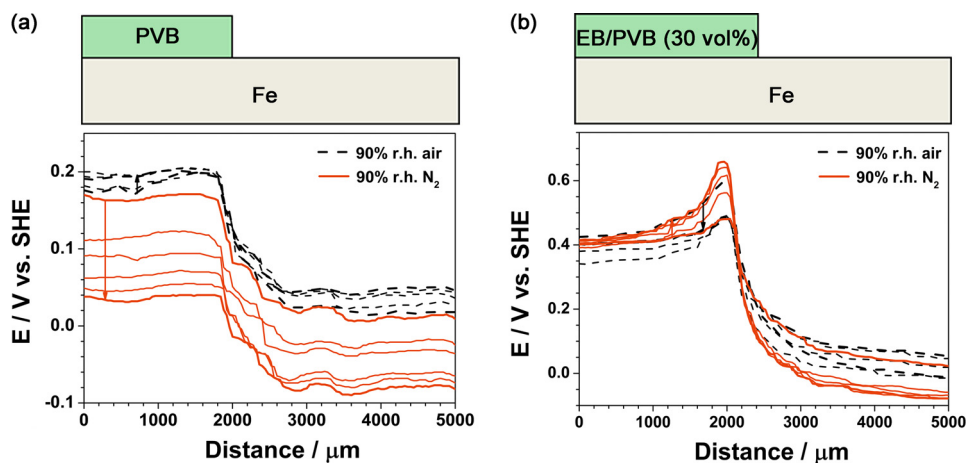


Fig. 1. Kelvin probe potential scans obtained in different atmospheres for the two polymer coated iron samples: (a) PVB and (b) 30%EB/PVB. The arrow shows the progression direction.

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