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Novel conducting polymer based composite coatings for corrosion protection of zinc

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ABSTRACT

The application of conducting polymers on zinc tends to result in an electronically highly insulating interface leading even to Fermi-level misalignment at the polymer/metal interface. This makes the conducting polymers electrochemically inactive. To prevent this Fermi-level misalignment, carbon black was introduced as conductive spacer between the conducting polymer and the zinc into composite coatings of poly (3,4-ethylenedioxythiophene) (PEDOT) nanoparticles and a polyvinyl butyral (PVB) binder. It was found that the carbon black not only enabled electronic contact between zinc and the PEDOT, but also increased the amount of electrochemical available PEDOT in the coating, by supplying the necessary conductive pathways.

1. Introduction

Great efforts are made to understand and develop a variety of strategies to protect metals against corrosion. One of the most effective ways for corrosion inhibition relies extensively on hexavalent chromium compounds used as additives to protective coatings. However, due to the carcinogenic toxicity of hexavalent chromium it is now stepwise forbidden, which has resulted in intense research for possible alternatives [1–3].

Conducting polymers (CPs) are quite promising for use as corrosion inhibiting additions to organic protective coatings [4–7]. In the 1980s, Mengoli et al. [8] and DeBerry [9] firstly proposed the possibility for steel corrosion protection by polyaniline (PANI), which was assumed to improve the quality of the passive layer on the steel by anodic polarization. Armelin and co-workers [5] compared the anticorrosive performance imparted by different CPs, namely PANI, polypyrrole (PPy) and PEDOT, when they are utilized as additives in the formulation of conventional epoxy paints. They found the coatings based on PEDOT/epoxy and PANI/epoxy significantly more protective against steel corrosion than the EP-standard paint. PEDOT, one of the polythiophene derivatives, is already extensively investigated for corrosion protection [10–13] due to its good thermal and electrochemical stability, ease of processing as well as environment-friendly property [14].

However, despite of all positive reports on CPs for corrosion protection, their application is not without problems [15–17]. Continuous coatings of conducting polymer may disastrously fail in the presence of a larger defect and may even cause an enhancement of corrosive attack [15]. Only when used as additives in composite coatings a safe use will be possible [15] provided that they promote the formation of a passive metal surface at the coating/metal interface [17–19]. Another problem is that CPs applied on zinc lead to the formation of an insulating layer at CP/metal interface resulting in electronically decoupling (Fermi-level misalignment) between the CP and the metal, leading to a seemingly too low potential. Williams et al. [18,19] and Nazarov and Thierry [20] also observed very low potentials when the coatings based on CPs were used on zinc, which can be explained by Fermi-level misalignment [17,21]. Consequently the CP is incapable of sensing the potential decrease occurring when the metal changes from passivity to active corrosion [15,17,21,22]. This may lead to an improved corrosion protection on zinc [23], but only by a passive and not by an active function as targeted here. To avoid the possibility of a Fermi-level misalignment, decoration of the CP particles with conductive nanoparticles, serving as conductive spacers between the CP and the zinc, is a reliable way to ensure electronic contact at the CPs/metal interface [21,22]. However, this makes the

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synthesis of the CPs more complicated and might be too cost intense for the commercial production of these decorated CP particles.

In this work as a possible alternative carbon black (CB), a good conductor, was directly added together with the PEDOT nanoparticles to the PVB binder. The resultant composite coatings with different CB concentrations were characterized and investigated in respect to their corrosion, i.e. corrosion driven delamination, performance. The anticorrosive properties and delamination kinetics of the composite coatings were evaluated in humid atmosphere by Scanning Kelvin Probe (SKP) technique.

2. Experimental section

2.1. Materials

3,4-Ethylenedioxythiophene monomer (EDOT, 97%), absolute ethanol, carbon black (99.95%), potassium chloride (KCl) and polyvinypyrrolidone (PVP, M_w: 10,000) as well as PVB ($M_w \approx$ 50,000–80,000 g mol^{-1}) were purchased from Sigma–Aldrich. Ammonium persulfate (APS, ⩾98%) was supplied by Merk. Acetonitrile (⩾99.93%) and phosphoric acid (⩾98%) was obtained from Fluka. All of the reagents were used directly as received without further purification. All aqueous solutions were obtained by using purified water from a USF ELGA water purification system (conductivity of less than 0.055 μS cm^{-1}).

Zinc sheets with a thickness of 1.5 mm (99.95%) were supplied by Goodfellow and cut for corrosion experiments to specimens with a dimension of 20 × 10 mm. The zinc sheets were ground with up to 1000 grit SiC paper, were cleaned thoroughly by rinsing them for 10 min in ethanol in an ultrasonic bath, and then dried in a nitrogen stream. Gold plates were prepared by evapourating 150 nm gold onto cleaned glass substrates.

2.2. Synthesis procedure for PEDOT

PEDOT nanoparticles were prepared by chemical polymerization. 2.152 g PVP was firstly dissolved in a mixture solution of water and acetonitrile (4:1, *v*/*v*) in a conical flask and stirred for 10 min under ultrasonic irradiation to mix uniformly. Then 1.28 ml EDOT monomer was slowly dripped into the mixture solution and ultrasonicated for another 30 min to obtain well-dispersed suspensions. Thereafter, 0.93 ml 0.05 M phosphoric acid was introduced, and APS aqueous solution were further added into the above mixture step by step whilst stirring to make 400 ml mixture and then left for 48 h at ambient temperature to undergo the polymerization. The molar ratio of APS to EDOT was 2:1. Subsequently, the resultant dark solid product was isolated by centrifugation and washed several times with ethanol, and followed by a mixture of water and ethanol (1:1, *v*/*v*) to remove the residual reagents until the supernatant fluid appears colorless and transparent. Finally, the resultant product was collected and dried at room temperature of 80 °C for 24 h and black fine powder of PEDOT nanoparticles were obtained.

2.3. Coating preparation

The composite dispersions were obtained from a mixture of CB blended with PEDOT (with a concentration of 17 μg μL^{-1}) in 0.5 ml ethanol. Subsequently, 1 ml 14 wt.% PVB ethanol solution was added into the above-obtained mixture. The concentrations of CB in the composite dispersions were 1.7, 3.3, 6.7 and 13.3 μg μL^{-1}, respectively. Then the mixtures were ultrasonicated for 20 min and kept stirring for more than 3 h at room temperature. The PEDOT/PVB dispersions with different CB concentrations were directly drop-casted on zinc and gold specimens, respectively, giving an average amount of 50 μL cm^{-2} and dried at 60 °C for 30 min. 14 wt.% PVB dissolved in ethanol was spin-coated once at 3500 rpm on the resultant PEDOT/CB/PVB films and dried at 60 °C for 1.5 h. The thickness of the coatings and the distribution of particles inside the coating were checked by scanning electron microscopy at cross sections of the samples (Fig. 6). The thus prepared coatings were found to have a thickness of about 10–15 μm. The concentration of each component in the PEDOT/CB/PVB composite coating is listed in Table 1.

Table 1
The concentration of each component in the PEDOT/CB/PVB composite coating.

Sample	PEDOT (wt.%)	CB (wt.%)	PVB (wt.%)
1	15.5	0	84.5
2	15.2	1.5 (1.7 μg μL^{-1})	83.2
3	15.0	2.9 (3.3 μg μL^{-1})	82.1
4	14.6	5.7 (6.7 μg μL^{-1})	79.7
5	13.8	10.8 (13.3 μg μL^{-1})	75.4

2.4. SKP measurements

In order to initiate the cathodic delamination progress an artificial defect was applied at the edge of the coating system with a scalpel and the resulting exposed area of zinc was ~10 mm^2 (about 1 × 10 mm^2). The defect was filled with 10 μL of 1 M KCl and the samples were subsequently introduced into the SKP chamber at 90–92% relative humidity. Delamination experiments were carried out with a commercial SKP system from KM Soft Control (Wicinski–Wicinski GbR, Wuppertal, Germany) with a 100 μm NiCr tip. The SKP tip was calibrated with saturated Cu/$CuSO_4$ solution and all potentials are given versus the standard hydrogen electrode (SHE) [24]. For monitoring the evolution of the corrosion potential at the interface between zinc and the coating the SKP tip was scanned in an area extending from close to the defect to a distance 6000 μm away. The progress of the cathodic delamination was monitored and analyzed according to the procedure described in Ref. [25].

2.5. Current measurements

Current measurements correlated to the reduction of active PEDOT in the composite coatings were performed by using a Voltcraft VC-840 digital multimeter. The active charge during PEDOT reduction of each coating was calculated by integrating the measured galvanic current over time. All experiments were first started in nitrogen atmosphere and the progress of the reduction of the PEDOT was measured, then the atmosphere was switched to air and the resulting coating delamination was measured.

A set-up as schematically shown in Fig. 1 was applied. By using an inert substrate (here gold) for the coating it was ensured that no anodic reaction occurs at the coated area. The cathodic polarization of the edge of the coated gold sample was achieved by establishing electronic contact with iron immersed in the electrolyte of the model defect site (see Fig. 1). This separation of anodic (iron dissolution) and cathodic (PEDOT reduction, if just nitrogen atmosphere is used, and PEDOT reduction plus oxygen reduction, if the experiment is carried out in air) reactions enables to measure the galvanic current between the artificial defect and the coating. The galvanic reaction takes place as long as the circuit is closed. The progress of coating reduction or reduction + delamination can be monitored by SKP. The reactions in nitrogen and air are shown as follows:

Anodic reaction:

$$N_2 \text{ or Air}: \quad Fe \rightarrow Fe^{2+} + 2e^- \tag{1}$$