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# On the development of polypyrrole coatings with self-healing properties for iron corrosion protection

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**Abstract**

This paper presents studies on the efficacy and on the limits of polypyrrole (Ppy) doped with either $MoO_4^{2-}$ or $[PMo_{12}O_{40}]^{3-}$ as self-healing corrosion protecting coatings. The kinetics of the cathodic delamination were studied by means of the Scanning Kelvin Probe (SKP). This method, in combination with cyclic voltammetry, UV–visible spectroscopy (UV–vis) and X-ray photoelectron spectroscopy (XPS), shows a potential driven anion release from the Ppy coating that results in an inhibition of the corrosion process taking place in the defect. Thus, an intelligent release of inhibitor occurs only when the potential at the interface decreases. Inhibitor anions are released only due to an active defect. However, the release mechanism can be easily negatively affected by the presence of small cations and/or by too high pH values at the buried interface. Hence, such a self-healing coating has to be carefully designed in order to ensure an effective performance.

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## 1. Introduction

In the last 20 years, in numerous publications, intrinsically conducting polymers (ICPs) have been controversially discussed as possible corrosion preventing additions to organic layers [1–4]. One of the reasons for the reported discrepancies is that most papers are focused just on very restricted aspects of corrosion. For instance, an ICP containing coating might be very effective in preventing corrosion in pin holes, while the same coating might fail disastrously in the presence of larger defects [4–6]. Quite numerous possible corrosion protection mechanisms are proposed [7–15]. According to Barisci et al. [16] ICPs might be used as intelligent release systems for corrosion inhibitors on demand. In this work was for the first time pointed out that the polymer could be reduced and consequently dopants could be set free as a result of a galvanic coupling between the corroding metal (iron) and ICP (polyaniline). A possible mechanism for the case of polyaniline was also described by Kendig et al. [17]. Such a coating which releases anions only in the case of corrosive attack but prevents them from being leached out or being released by ion exchange processes, would be a self-healing coating. Nevertheless, no results showing successful dopant release, as a consequence of electrochemical ICP reduction through the corrosion in the defect have been reported until now.

This paper shows that on the basis of polypyrrole coatings, which show a electrochemical release of inhibitor anions can be prepared. Even unusually large defects can be passivated because the switch for anions release is the decrease in potential at the metal/polymer interface during the delamination. If the defect is smaller less coating will delaminate, if it is larger more coating delaminates until successful passivation.

Some results concerning a positive influence of aminotris(methylene phosphonic acid) (ATMP) anion doped polyaniline (PANI) on the corrosion behaviour of mild steel have been reported by Kinlen et al. [18,19]. Release of ATMP from the PANI and formation of stable adducts with iron ions have been observed. These adducts could lead to the passivation of pinholes. According to the proposed mechanism, the ATMP is released as a consequence of polyaniline–emeraldine salt (PANI–ES) reduction to polyaniline–leucoemeraldine salt (PANI–LS). The number of anions in the polymer chain does not change in the mentioned reaction [16,17,20] and this might be one of the critiques concerning this proposed mechanism. Additionally, it is worth of mentioning that the PANI–LS form is stable only at low pH and that during cathodic delamination strongly alkaline pH prevail. Hence, a high pH induced deprotonation of PANI–ES to the form of polyaniline–emeraldine base (PANI–EB) or reduction to the form of polyaniline–leucoemeraldine base (PANI–LB) is more likely to take place under these conditions. Also, in the most recent publications [21,22] concerning this subject, no observations clearly explaining the mechanism of anion release from PANI–ES in corrosion experiments have been reported.