

Grazyna Paliwoda-Porebska · Michael Rohwerder ·
Martin Stratmann · Ursula Rammelt ·
Le Minh Duc · Waldfried Plieth

Release mechanism of electrodeposited polypyrrole doped with corrosion inhibitor anions

Received: 11 August 2005 / Accepted: 9 November 2005 / Published online: 4 May 2006
© Springer-Verlag 2006

Abstract Scanning Kelvin probe and electrochemical impedance spectroscopy were used to study the release behaviour of inhibitor anions doped in polypyrrole film (e.g. molybdate, 3-nitro salicylate). The polypyrrole coatings were formed on mild steel and zinc substrates in aqueous solution. It was shown that the release behaviour of the molybdate and 3-nitro salicylate anions depends on the size of cations in the electrolyte. The delamination is determined with the migration and incorporation of small cations.

Keywords Polypyrrole · Corrosion inhibitors · Release system · Scanning Kelvin probe (SKP) · Electrochemical impedance spectroscopy (EIS)

Introduction

For many years, coatings based on intrinsically conducting polymers (ICPs) have been controversially discussed as being useful for corrosion protection of active metals such as iron, mild steel, zinc or aluminium. It seems widely accepted that ICPs can decrease the corrosion rate of active metals, but they seem to work only under certain special conditions. Until now there have been many attempts to explain the corrosion protection mechanism. The most discussed aspect of protection by ICPs is an active protection including anodic protection, the mediation of electron transfer and the role of ICPs as oxygen reduction catalysts [1–5]. However, an ICP film alone cannot protect an active metal completely. Rammelt et al. [6] showed that

an ICP film does not act as a redox mediator, passivating the steel substrate within the defect and reoxidising itself by dissolved oxygen, although Michalik and Rohwerder showed that, under special cyclic conditions, this might work [7]. Recently, a more promising concept has been proposed [8–12]. In oxidised ICP, anions are incorporated to compensate the positive charge on the oxidised polymer backbone. These anions may be released by the reduction of the polymer, induced by the oxidation of the metal in the corroding defect. If these anions have corrosion-inhibiting properties, their release could passivate the defect. Up to now, no convincing experimental proof for this mechanism has been provided. Kinlen et al. [9, 10] and Kendig et al. [11] observed the release of corrosion-inhibiting anions from polyaniline coatings in contact with a corroding defect, but in fact, in the case of polyaniline, the mechanism for the anion release is not the reduction of the polymer but its deprotonation due to an increase of pH.

Recently, Paliwoda-Porebska et al. presented the first proof of truly electrochemical anion release from polypyrrole (Ppy)-containing composite coatings [13]. In these experiments, even a comparatively large defect could be passivated and further coating delamination could be successfully stopped. However, 1–2 mm of coating had to delaminate before enough anions were released into the defect to be sufficient to stop the corrosion. The main reason for this is the limited amount of active Ppy in the used composite coatings. Hence, the logical approach would be to use coatings of 100% conducting polymer to maximise the amount of available inhibitors.

In the current paper, a critical analysis on the efficacy of, and also the problems involved with, electropolymerised Ppy films on iron and zinc substrates is presented.

Experimental

Synthesis Ppy films were formed potentiostatically on Pt electrodes for electrochemical impedance spectroscopy (EIS) measurements in an aqueous solution of 0.1 M pyrrole. Ppy(MoO₄) films were prepared at E=0.8 V vs

G. Paliwoda-Porebska · M. Rohwerder · M. Stratmann
Max-Planck-Institut fuer Eisenforschung,
Max-Planck-Str. 1,
Duesseldorf, Germany

U. Rammelt · L. M. Duc · W. Plieth (✉)
Department of Chemistry, Institute of Physical Chemistry
and Electrochemistry, Dresden University of Technology,
Mommensenstrasse 13,
01062 Dresden, Germany
e-mail: waldfried.plieth@chemie.tu-dresden.de

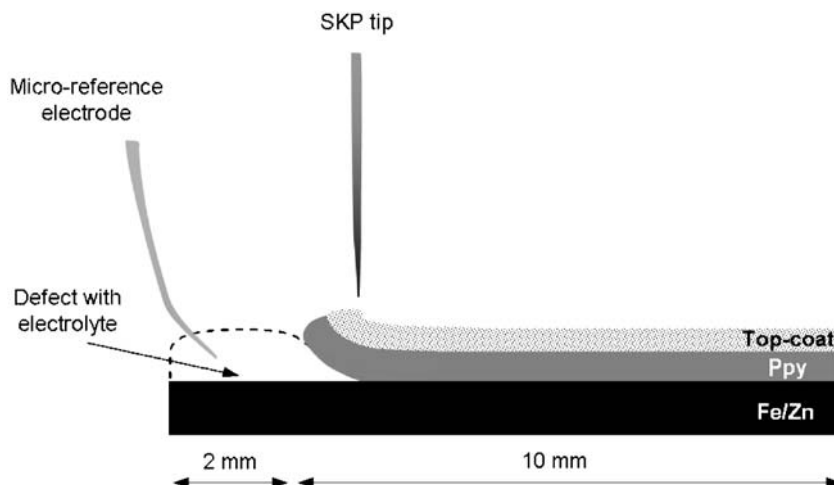
saturated calomel electrode (SCE) using 0.01 M sodium molybdate (pH=4.8), and Ppy(3Nisa) films at $E=1.0$ V vs SCE using 0.01 M 3-nitrosalicylic acid (pH=2.5) as supporting electrolyte.

For corrosion tests, Ppy films were formed on mild steel and zinc at a current density of 1.5 mA/cm^2 in an aqueous solution of 0.1 M pyrrole and 0.01 M sodium molybdate solution for mild steel [Ppy(MoO₄)], and in an aqueous solution of 0.3 M pyrrole and 0.01 M 3-nitrosalicylic acid for zinc [Ppy(3Nisa)]. After forming, the samples were rinsed in distilled water and dried in nitrogen atmosphere. The thickness of Ppy film was about $1 \text{ }\mu\text{m}$ controlled with total passed charge (assumed $0.4 \text{ C/cm}^2 \cdot \mu$) [14].

Electrochemical set-up The voltammetric experiments of Ppy films were carried out by using an EG&G-263A model potentiostat/galvanostat with a potential sweep rate of 1 mV/s . The open circuit potential (OCP) was followed vs time and EIS measurements were made at different potentials using the IM6 impedance measurement system of ZAHNER-elektrik. The frequency range analysed was $100 \text{ kHz}-1 \text{ Hz}$. The electrolyte was 0.1 M tetrabutylammonium bromide (TBABr) and 0.1 M NaCl solution. All potentials are referred to the SCE.

SKP experiments The SKP used in this work was constructed in the Max Planck Institute for Iron Research. The electronic part of the setup, consisting of a pre-amplifier, a lock-in-amplifier and an integrator, was provided by commercial suppliers. A similar SKP setup has been successfully used in other research projects (see e.g. [15–17]). The used SKP tip has a diameter of $100 \text{ }\mu\text{m}$. To perform SKP experiments on the delamination behaviour, Ppy coatings were electrodeposited on a part of the iron or zinc samples, while on another part, an artificial defect was prepared (Fig. 1). For some of the SKP experiments, Ppy films electrodeposited on Au (evaporated on glass) were used. To perform the delamination experiments, an iron plate, which functioned as a defect, was connected with the Au substrate (Fig. 2). This kind of Au sample/iron defect set up has already been successfully used [7].

Fig. 1 Preparation of iron and zinc substrates, coated with Ppy films, for the SKP experiments



To avoid difficulties resulting from significant folding of the coatings during the delamination experiments, an additional polyacryl resin top-coat (Badische Anilin und Soda Fabrik) was applied to all Ppy films studied with the SKP.

In the defect, 0.1 M KCl or 0.1 M tetrabutylammonium chloride solution was injected. All SKP measurements were performed in a humid atmosphere (RH=93–95%), which was controlled during the experiment. After the SKP experiments, the delaminated Ppy coatings could be easily peeled-off from the metal surface. Then, an X-ray photoelectron spectroscopy (XPS) analysis of the delaminated Ppy films and the sample surface was performed. With the use of a micro-reference electrode [18], the OCP in the defect was measured simultaneously to the SKP measurement.

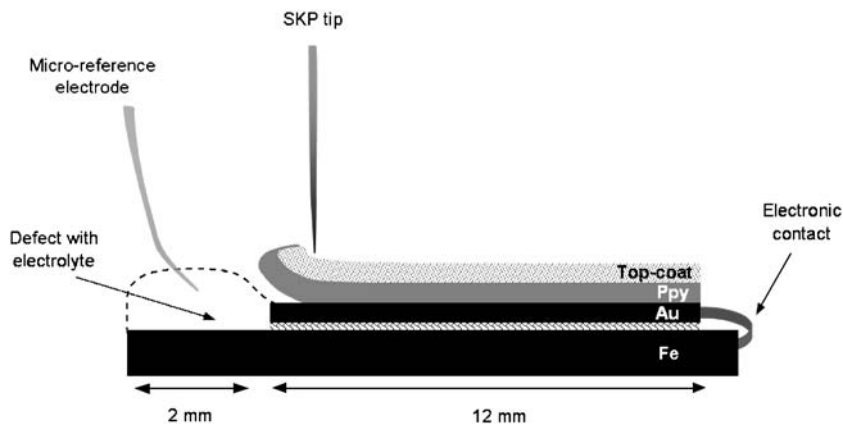
Results and discussion

Anion/cation transport during reduction

The corrosion protection of Ppy films containing inhibitor anions as dopant anions starts with the reduction of the polymer film, induced by the oxidation of the metal in a corroding defect. If the dopant anions are small enough, they are released from the Ppy film during reduction for charge compensation. In the case of large anions, the charge compensation takes place preferentially by cation insertion. In many cases, a mixed anion/cation transport is observed depending on the size of the dopant anions and the electrolyte solution used in reduction experiments. The ion exchange behaviour has been investigated intensely by electrochemical quartz crystal microbalance (EQCM) [19–23] and EIS measurements [24–27].

Different inhibitor anions were tested: molybdate for mild steel and different nitrosalicylic acids for zinc. Müller and Langenbucher [28] have found that nitrosalicylic acids, which have a nitro-group ortho to a hydroxy-group, are effective inhibitors for zinc flakes used as pigments in water-borne paints. The inhibiting effect can be explained with the formation of chelate complexes with Zn(II).

Fig. 2 Preparation of the gold (evaporated on glass) substrate, coated with Ppy film, for the SKP experiments



However, as can be seen from OCP–time measurements (Fig. 3), a marked effect is observed only with 3-nitrosalicylic acid. The OCP of pure zinc is shifted at about 0.45 V to more positive values, compared with salicylic acid without nitro-group.

If a Ppy film doped with molybdate as inhibitor anion is reduced, the exchange behaviour depends on the ions present in the electrolyte solution. Reducing the Ppy film in a solution with large cations, such as TBABr, only anion release takes place, whereas, in NaCl solution, a mixed anion/cation transport is observed with EQCM measurements [22].

These results were confirmed by EIS measurements [27]. The impedance spectra were obtained during the reduction of Ppy(MoO₄) in 0.1 M TBABr and 0.1 M NaCl solution. During reduction the conductivity of Ppy (MoO₄) films decreases, as do the values of the capacitance. The decrease of capacitance is only observed if the dopant anion can release the Ppy film during reduction [22, 27]. As can be seen in Fig. 4, the release of molybdate anions is possible in both electrolyte solutions, but in a NaCl solution, the decrease of capacitance is smaller than in a TBABr solution. In a NaCl solution, the small sodium ion can be incorporated into the polymer

matrix very easily so that a mixed anion release/cation insertion takes place. With 3-nitrosalicylate anions, the same behaviour is observed, but in NaCl solution, the decrease of capacitance (that means the release of 3-nitrosalicylate anions) is smaller than in the case of molybdate anions. The question now is: Is the mobility of the inhibitor anions molybdate and 3-nitrosalicylate high enough for stopping the corrosion?

Repair effect by inhibitor anions

OCP measurements

The OCP measurements show that the efficacy of Ppy films for corrosion inhibition can be improved by using inhibitor anions as dopant anions. Doped Ppy films formed directly on mild steel or zinc were immersed in a 0.1 M NaCl solution as corrosive medium and the OCP was followed vs time. A typical curve for Ppy(3Nisa) on zinc is presented in Fig. 5. Initially, the OCP was about 0.1 V and corresponded to the redox potential of Ppy(3Nisa), also existing for a Ppy (3Nisa)-coated Pt electrode. Zinc was in its passive state. After 1.5 h the potential decreased to a second plateau at

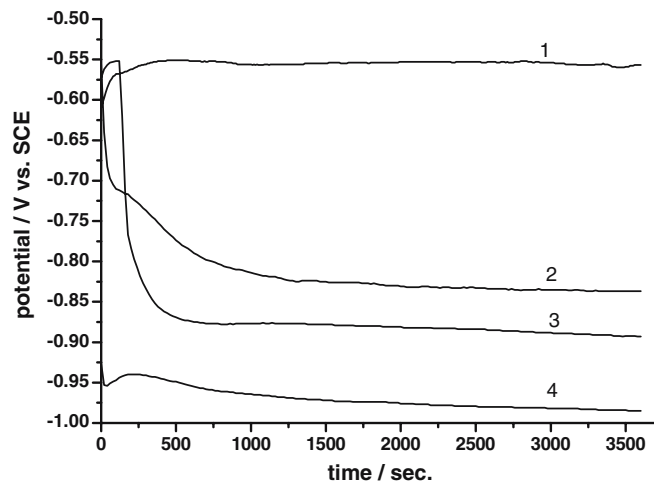


Fig. 3 OCP-vs-time measurements of Zn in different 0.01-M electrolyte solutions at pH=2.5 3-nitrosalicylic acid (1), 5-nitrosalicylic acid (2), 3,5-dinitrosalicylic acid (3), salicylic acid (4)

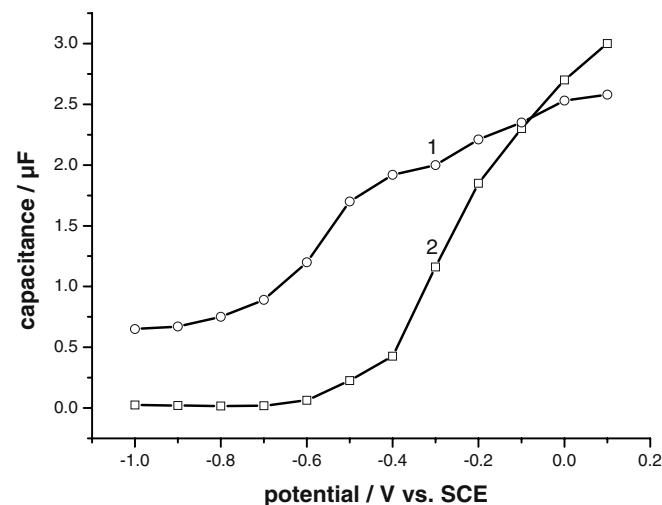


Fig. 4 The change of Ppy(MoO₄) capacitance during reduction in 0.1 M NaCl (1) and 0.1 M TBABr (2)

about -0.4 V. At this stage the chloride ions have reached the zinc surface and the corrosion reaction can start, inducing a partial reduction of the Ppy(3Nisa) film. The potential of -0.4 V is in the range of the potential of pure zinc immersed in 3-nitrosalicylate (see Fig. 3), which means that zinc dissolution is inhibited by the formation of a chelate complex with Zn(II). Bode plots recorded during the second plateau confirm this behaviour (see Fig. 6). The resistance of Ppy(3Nisa) increased and the capacitance decreased slightly, indicating the release of 3-nitrosalicylate anions. However, the mobility of 3-nitrosalicylate was not high enough to protect zinc for a longer time. The protection time, which was previously defined as the time during which the OCP of the covered metal remains in the passive state before it drops down to the corrosion potential of the unprotected metal, was shorter than the protection time of Ppy(MoO₄) films on mild steel [27]. Compared with Ppy(MoO₄) films, the short first plateau could be attributed to a relative high porosity of Ppy(3Nisa) films, whereas the shorter second plateau was connected with the low mobility of 3-nitrosalicylate anions. However, it should be mentioned that 3-nitrosalicylate as supporting electrolyte is, until now, the only system where electro-deposition of pyrrole on zinc can take place without special pre-treatment.

SKP measurements

In Fig. 7, potential profiles, as measured by Scanning Kelvin probe (SKP) during the delamination of Ppy(MoO₄) film from an iron substrate, are shown. The high potentials on the upper right side indicate the still-intact, unreduced coating. From the border to the defect at $d=0$, a front of lower potentials proceeds into the coating. In equivalence to the SKP delamination profiles measured for the delamination of non-conducting organic coatings, these low potentials may be interpreted as an indication for coating delamination: Where the coating is delaminated,

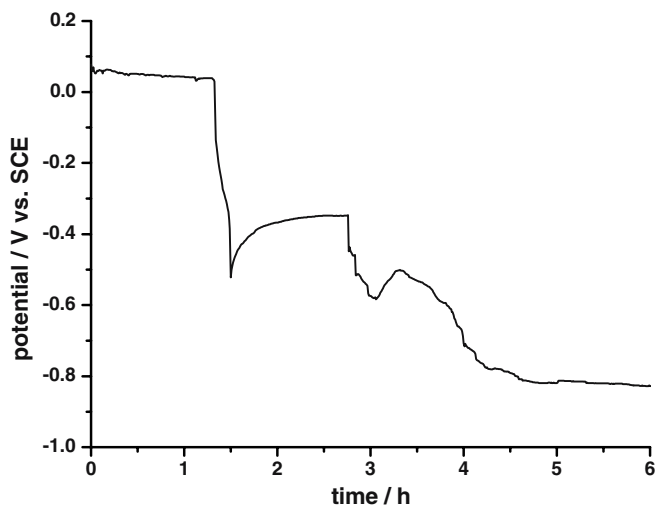


Fig. 5 OCP-vs-time curve for zinc covered with Ppy(3Nisa) in 0.1 M NaCl

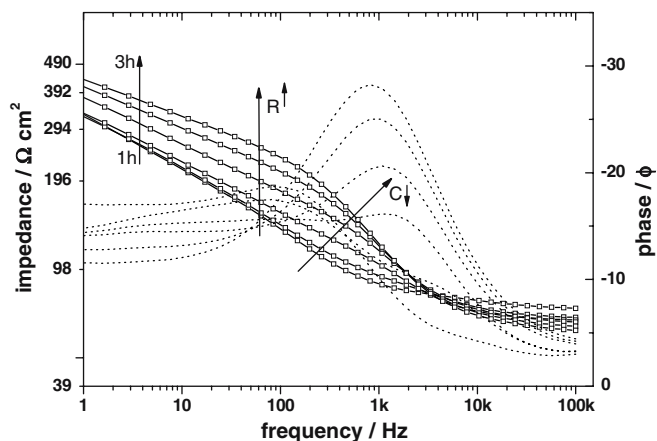


Fig. 6 Bode plots obtained on the second plateau of the OCP vs time curve for Ppy(3Nisa) on zinc (see Fig. 3)

the electrode potential at the interface is pulled down to the corrosion potential in the defect, as the Ohmic resistance along the delaminated interface is low [29]. However, it has to be taken into account here that in the case of conducting redox polymers, it is the Nernst potential, determined by the ratio of oxidised to reduced sites in the conducting polymer backbone, that is measured, similar to the potential measured on iron oxides, which is determined by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio [30]. So, first of all, it is the reduction of Ppy coating that is observed here. Because the corrosion potential in the defect is about -0.45 V vs standard hydrogen electrode (SHE), this value should determine the limit for the Ppy reduction. Indeed, this is about the value that is measured on the reduced coating. At this low potential the Ppy coating is nearly fully reduced and has become non-conducting. Hence, in the area where the coating is reduced, it should behave like a normal non-conducting coating. The low potential would then also indicate that oxygen is reduced, and hence, the coating is delaminated.

Now, the idea was that the molybdate anions stored in the coating would be released during the coating's

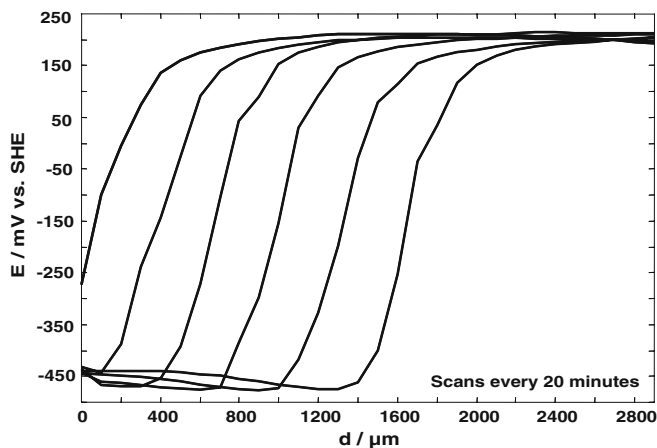


Fig. 7 SKP delamination profiles of Ppy(MoO₄) coating electro-deposited on iron. Experiment performed with 0.1 M KCl in the defect

reduction and stop the corrosion in the defect, thus preventing further reduction and delamination of the coating. But, contrary to similar experiments performed with composite coatings [13], no indication of defect passivation can be deduced from the potential profiles, as no increase in potentials near the defect, and also no slowing-down of the progress of the delamination front, can be observed.

The potential evolution in the defect was measured simultaneously with the delamination profiles. Indeed, throughout the experiment, the measured corrosion potential in the defect remained constant at the corrosion potential of actively corroding iron of about -0.45 V vs SHE, which corresponds to the potential measured in the delaminated area.

Because molybdate is a very powerful corrosion inhibitor for iron, and concentrations as low as 10^{-5} M cause a significant anodic shift of the corrosion potential, the observed absence of any molybdate-induced passivation of the defect was a surprise, as the molybdate contained in the reduced Ppy should be more than sufficient for an efficient defect passivation. A similar experiment carried out with a Ppy coating doped with an anion that is not a corrosion inhibitor led to more or less the same delamination profiles [7].

After the experiment, the delaminated coating was pulled off the iron substrate and the coating's underside was analysed by XPS. The amounts of molybdate determined in the coating before and after the delamination were 3.4 and 2.8%, respectively. This shows that no significant release of molybdate occurred. Further XPS analysis showed that instead, potassium cations were incorporated into the Ppy (see Figs. 8 and 9). Anion release and cation incorporation are competing parallel reactions during the reduction of Ppy. However, it is surprising that the cation incorporation nearly totally suppressed the anion release.

Most likely, cation transport is much easier in the reduced Ppy than anion transport. Because, in the electro-

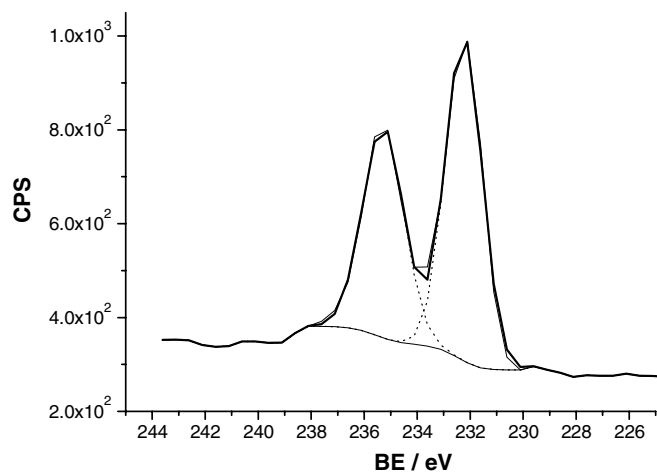


Fig. 8 XPS spectra of molybdenum found in the delaminated Ppy (MoO_4) coating (peaks positions 3d3/2 235.3 eV and 3d5/2 232.2 eV)

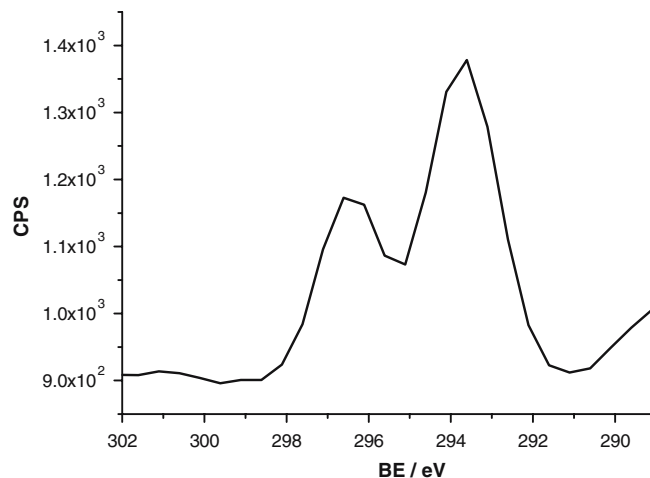


Fig. 9 XPS spectra of potassium found in the delaminated Ppy (MoO_4) coating (peaks positions 2p1/2 296.5 eV, 2p3/2 293.71 eV)

chemical experiment, transport occurred only over a few microns, while in the case of delamination it occurs over several hundred microns, this might result in the observed dominance of cation incorporation for charge compensation during coating reduction. This total dominance of cation incorporation was observed for all tested electro-polymerised Ppy coatings doped by molybdate, tosylate or perchlorate [7]. To investigate this effect further, experiments with very large cations in the defect were carried out. Figure 10 shows the delamination curves for a Ppy coating doped with molybdate equivalent to the curve in Fig. 4. In this case, right from the beginning, the reduction and delamination proceeded much slower than it did in the presence of the big cations in the defect. Because this slower delamination velocity was observed at once, it was obviously due to a lack of small cations for fast charge compensation during delamination, i.e. the reduction of the polymer was slowed down by slow charge compensation. XPS analysis of the coating after the delamination experiment showed that the bulky tetrabutylammonium cation used in the defect was not incorporated, which indicates that it was too big for incorporation into the Ppy. All charge compensation then occurred via the release of the molybdate anions, which, obviously, was much slower than the incorporation of the small potassium cations.

The evolution of the corrosion potential in the defect now shows that after about 5 to 10 h, a significant increase of the corrosion potential by about 80 mV takes place (Fig. 11). This does not seem to be much, but during this period only an extremely small stripe of the Ppy coating near the defect border was slightly reduced (notice that there was 5 h between consecutive curves; after 5–10 h, a stripe of less than 250 μm was only partially reduced). Hence, although anion release took place, it was too slow to fully passivate the defect. But because the driving force for delamination is the potential difference between intact coating and corrosion potential in the defect [29], even this small increase, causing a decrease in the potential difference by about 20%, should result in a decrease of coating delamination. In the contrary, after about 20 h, the

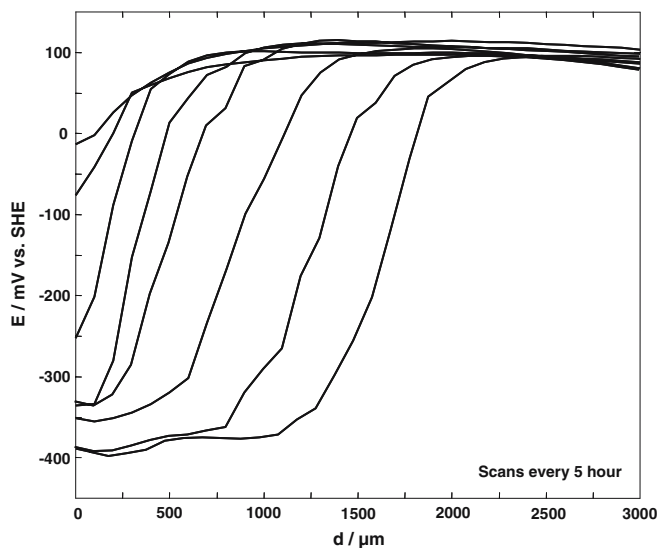


Fig. 10 SKP delamination profiles of Ppy(MoO₄) coating electro-deposited on iron. Experiment performed with 0.1 M tetrabutylammonium chloride in the defect

delamination even seemed to speed up. This falls together with the time required for the full reduction of the Ppy that was nearest to the defect border; up to the first 20 h, only partial reduction could be observed. By pulling the coating off the iron substrate, it was observed that the adhesion in the fully reduced area was totally lost, indicating that delamination requires full reduction of the coating. Full delamination means that electrolyte penetrates into the interface. For coatings with very weak adhesion, the involved mechanical stresses at the interface may result in a significantly increased delamination velocity, sped up by these mechanical forces [31]. It is assumed that the adhesion of the Ppy to the iron substrate is indeed quite weak.

Hence, as soon as the first stretch of Ppy coating was delaminated, the undercreepage of the delaminated coating by electrolyte caused a mechanical breakdown of the

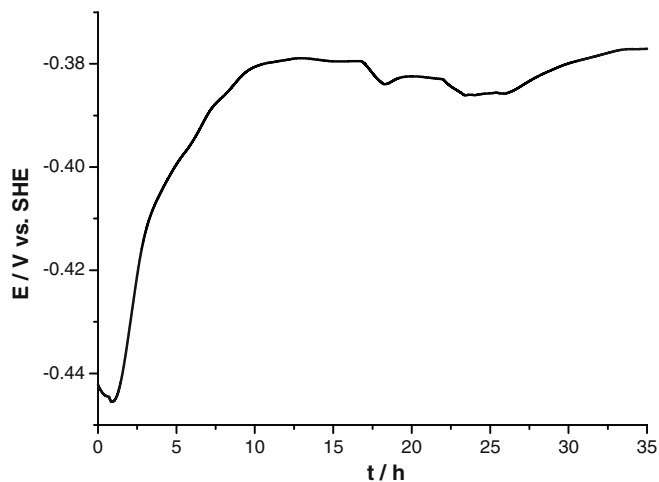


Fig. 11 Potential change in the defect during the delamination of Ppy(MoO₄) coating. Experiment performed with 0.1 M tetrabutylammonium chloride in the defect

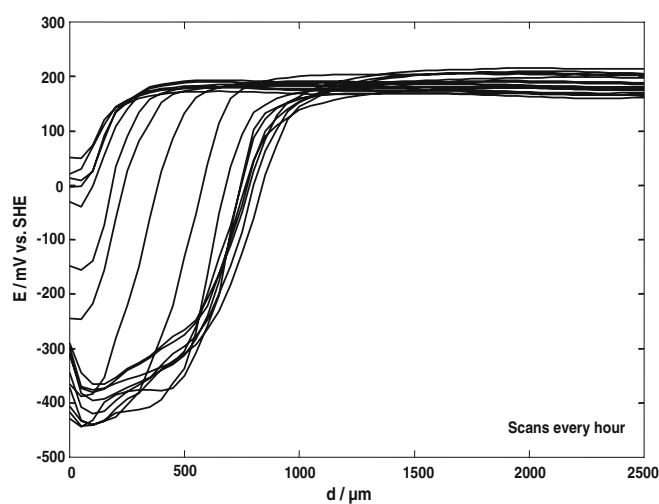


Fig. 12 SKP delamination profiles of Ppy(MoO₄) coating electro-deposited on Au. Experiment performed with 0.1 M tetrabutylammonium chloride in an iron defect

coating adhesion. Because the electrodeposition of Ppy on iron involves a pre-passivation of the iron surface by a molybdate layer and the adhesion of the Ppy to this layer seems to be the weak point, delamination experiments were carried out for Ppy coatings deposited on gold, in contact with a corroding iron defect (see also Fig. 2). In this case, the delamination profiles do indeed show a slowing-down of the delamination after about 10 h (Fig. 12), i.e. after the time required for the increase of corrosion potential in the defect. Obviously, in this case the adhesion between coating and substrate is much better, and the mechanical forces correlated to the undercreepage of the delaminated area, which are solely determined by the electrochemically driven delamination process, do not speed up the delamination process. Similar experiments have also been performed for 3-nitrosalicylate-doped Ppy films on zinc, because in immersion experiments, these coatings show significant corrosion protection.

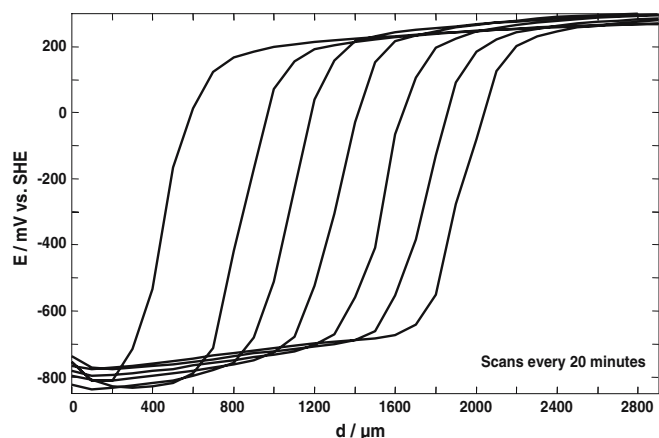


Fig. 13 SKP delamination profiles of Ppy(3Nisa) coating electro-deposited on zinc. Experiment performed with 0.1 M KCl in the defect

But, again, for a non-immersed sample in the case of delamination starting from a larger defect in the coating, no inhibition of corrosion in the defect and of the delamination itself could be observed (Fig. 13). The observed delamination rate is about 0.9 mm/h, which is basically the same as measured for the molybdate-doped Ppy film on iron. This indicates that, once again, the delamination rate is determined by the migration and incorporation of the potassium cations and not by the release of the inhibitor anions. Indeed, XPS analysis shows that the anions have not been released and that potassium was incorporated.

Conclusions

The results presented here show that the idea of corrosion-induced inhibitor release works for immersed samples with small defects, while for non-immersed samples, where just the defect is covered with a thin layer of electrolyte, the mechanism fails. The main difference between these two cases is that for immersed samples all the Ppy coating is available for immediate anion release, while for the delamination from an electrolyte-covered defect, only the Ppy first in contact with the defect border, and at later stages, the Ppy at the delamination front, could provide the inhibitor anions. Because the coatings are only a few microns in thickness, a larger scratch of several hundred microns in width would require the reduction of a similar stretch of coating to deliver the required amount of inhibitor anions. Over these distances, however, the incorporation of cations into the Ppy is the dominating process. Obviously, the transport of cations is much faster than that of anions.

Hence, pure Ppy coatings cannot inhibit delamination from larger defects. The fact that experiments on composite coatings, in which Ppy particles have been used as additives, show that, in these cases, a self-healing effect can be obtained [13] indicates that the fast cation transport is an inherent property of Ppy, precisely of reduced Ppy.

References

1. Nguyen TD, Keddani M, Takenouti H (2003) *Electrochim Solid State. Lett* 6:B25
2. Spinks GM, Dominis AJ, Wallace GG, Tallman DE (2002) *J Solid State Electrochem* 6:85
3. Lu WK, Elsenbaumer RL, Wessling B (1995) *Synth Met* 71:2163
4. Conroy KG, Breslin CB (2003) *Electrochim Acta* 48:721
5. Bernard MC, Joiret S, Hugot-Le Goff A, Phong PV (2001) *J Electrochem Soc* 148:B12
6. Rammelt U, Nguyen PT, Plieth W (2003) *Electrochim Acta* 48:1257
7. Michalik A, Rohwerder M (2005) *Z Phys Chem* 219:1547
8. Barisci JN, Lewis TW, Spinks GM, Too CO, Wallace GG (1998) *J Intell Mater Syst Struct* 9:723
9. Kinlen PJ, Menon V, Ding YW (1999) *J Electrochem Soc* 146:3690
10. Kinlen PJ, Ding YW, Silverman DC (2002) *Corrosion* 58:490
11. Kendig M, Hon M, Warren L (2003) *Prog Org Coat* 47:183
12. Hien NTL, Garcia B, Pailleret A, Deslouis C (2005) *Electrochim Acta* 50:1747
13. Paliwoda-Porebska G, Stratmann M, Rohwerder M (2005) *Corros Sci* 47:3216
14. Diaz AF, Castil JL, Logan JA, Lee WY (1981) *J Electroanal Chem* 129:115
15. Hausbrand R, Stratmann M, Rohwerder M (2003) *Steel Res Int* 74:453
16. Stratmann M, Feser R, Leng A (1994) *Electrochim Acta* 39:1207
17. Stratmann M, Streckel H, Kim KT, Crockett S (1990) *Corros Sci* 30:715
18. Hassel AW, Fushimi K, Seo M (1999) *Electrochem Commun* 1(5):180
19. Schmidt VM, Heitbaum J (1993) *Electrochim Acta* 38:349
20. Syritski V, Öpik A, Forsen O (2003) *Electrochim Acta* 48:1409
21. Grzeszczuk M, Kepas A, Zabinska-Olszak G (2004) *Electrochim Acta* 49:2405
22. Plieth W, Bund A, Rammelt U, Neudeck S, Duc LM (2005) *Electrochim Acta* 51:2366
23. Weidlich C, Mangold KM, Jüttner K (2005) *Electrochim Acta* 50:1547
24. Ren X, Pickup PG (1997) *J Electroanal Chem* 420:251
25. Ehrenbeck C, Jüttner K (1996) *Electrochim Acta* 42:1815
26. Rammelt U, Bischoff S, El-Dessouki M, Schulze R, Plieth W, Dunsch L (1999) *J Solid State Electrochem* 3:406
27. Rammelt U, Duc LM, Plieth W (2005) *J Appl Electrochem* 35:1225
28. Müller B, Langenbucher J (2003) *Corros Sci* 45:395
29. Rohwerder M, Stratmann M (1999) *MRS Bull* 24(7):43
30. Grundmeier G, Stratmann M (1999) *Appl Surf Sci* 141(1–2):43
31. Rohwerder M, Hornung E, Stratmann M (2003) *Electrochim Acta* 48(9):1235