

## Improvement of protection performance of polypyrrole by dopant anions

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### Abstract

Electropolymerisation of pyrrole on mild steel was carried out in 0.01 M sodium molybdate and 0.1 M pyrrole solution at constant current  $1.5 \text{ mA cm}^{-2}$ . The film is homogenous and adherent. The corrosion protection of polypyrrole films containing inhibitor anion molybdate as dopant anion was investigated with open circuit potential (OCP) in 0.1 M NaCl. The passivating effect of molybdate was demonstrated. The mobility of anion was investigated by cyclic voltammetry (CV), electrochemical quartz microbalance (EQCM) and electrochemical impedance spectroscopy (EIS) measurements.

### 1. Introduction

The use of intrinsically conducting polymers (ICP) as anticorrosion coatings has been proposed as a possible nontoxic replacement for chromate-based coatings. The application of ICPs takes place directly by electrodeposition on the active material such as mild steel, iron and aluminium or by coating of formulated solutions of these polymers. It was demonstrated that in many cases ICPs can decrease the corrosion rate of active materials, but that significant advances are necessary to increase the protection time, especially if the polymer films have small defects. Until now the mechanism of corrosion protection is not understood in detail. The main aspect of protection by ICPs discussed in the literature is an active protection including anodic protection, mediation of electron transfer and the role as oxygen reduction catalyst [1–5]. However, an ICP film alone cannot protect an un-noble metal completely. With a new galvanic coupling experiment we have investigated the ability of polymethylthiophene (PMT) electrochemically deposited on mild steel to delay the onset of corrosion within a small defect. It could be shown that the PMT film does not act as a redox mediator, passivating the steel substrate within the defect and reoxidizing itself by dissolved oxygen [6]. An improvement in corrosion performance should be possible, if special dopant anions are introduced into the polymer during synthesis. In some cases large anions are irreversibly incorporated into the positively charged polymer backbone in order to change the permselectivity from anionic to cationic

[7–9]. Large size anions like polystyrenesulfonate, sodium dodecylsulfate, polymolybdate or camphosulfonate cannot be exchanged during the redox process and therefore the penetration of aggressive anions like chloride is strongly reduced. This barrier effect does not work if the coating has small defects. In this case the dopant anion can help to passivate the steel surface within the defect if the anion is small and can release from the conducting polymer during reduction. The passivation is possible if the dopant anion can form an insoluble iron-dopant salt at the metal surface [10–15]. Kendig et al. [16] describe the corrosion protection of aluminium in chloride environments by inhibitor anions incorporated in polyaniline (Pani). The coatings are doped with one of the class of anions that inhibit the oxygen reduction reaction.

It is basically important to study and control the mobility of anions. These objectives were achieved by electrochemical quartz microbalance (EQCM) and electrochemical impedance spectroscopy (EIS) measurements combined with cyclic voltammetry (CV). The EQCM is a very sensitive method to control the change of mass during the electrochemical reduction of the ICP. The mass transport process can be connected to the electrical properties, especially the change of resistance and capacitance, observed with EIS.

In this contribution, the EQCM and EIS measurements combined with CV were used to study the redox behaviour of polypyrrole (Ppy) doped with molybdate (Ppy(MoO<sub>4</sub>)). In the presence of molybdate strongly adherent films can be formed directly on mild steel by

electropolymerization without any dissolution of metal. Molybdate was incorporated within the polymer during film formation as corrosion inhibitor. The corrosion protection given by molybdate is investigated by open circuit potential (OCP) – time measurements and potentiodynamic curves.

## 2. Experimental

The mild steel St-38 electrodes ( $20 \times 20 \text{ mm}^2$ ) were polished with 600 grit emery paper and then cleaned ultrasonically with ethanol. The electropolymerization was performed in a conventional three-electrode cell with a Pt gauze as counter electrode and the saturated calomel electrode (SCE) as reference electrode. The Ppy films were generated galvanostatically on the pre-treated mild steel surface at a current density of  $1.5 \text{ mA cm}^{-2}$  in an aqueous solution of  $0.1 \text{ M}$  pyrrole (from Aldrich 98%, keep at  $4^\circ \text{C}$  and distil in argon atmosphere before using) and  $0.01 \text{ M}$  sodium molybdate ( $\text{pH} = 4.8$ ). After forming, the sample was rinsed in distilled water and dried in nitrogen atmosphere. The film thickness was about  $1\text{--}1.2 \mu\text{m}$ . For investigation of the release behaviour of molybdate anion during the reduction of Ppy, the films were electrodeposited on Pt.

Cyclic voltammetry experiments of  $\text{Ppy}(\text{MoO}_4)$  films were carried out by using EG&G–263A Model potentiostat/galvanostat with a potential sweep rate of  $20 \text{ mV s}^{-1}$ . The aqueous electrolyte was  $0.1 \text{ M}$  tetrabutylammonium bromide ( $\text{N}(\text{Bu})_4\text{Br}$ ) solution purged with  $\text{N}_2$  before and during experiment.

EIS investigation was done by using the IM6 impedance measurement system of ZAHNER-elektrik. The frequency range analysed was  $100 \text{ kHz} - 0.1 \text{ Hz}$ . A  $\text{Ppy}(\text{MoO}_4)$  film deposited on Pt was reduced from  $0.1 \text{ V}$  to  $-1 \text{ V}$  (vs. SCE) in  $0.1 \text{ M}$  ( $\text{N}(\text{Bu})_4\text{Br}$ ) after a waiting time of  $10 \text{ min}$  at each potential.

In EQCM measurements, the working electrode was an 'AT-cut'  $10 \text{ MHz}$  quartz crystal ( $15 \text{ mm}$  in diameter) with Au electrodes on a chromium adhesion layer provided by KVG (Neckarbischofsheim, Germany) [17]. They were held between two O-ring gaskets (active area  $0.23 \text{ cm}^2$ ). A cylindrical Teflon cell was used to fix the quartz crystal at its bottom. One side of the working electrode facing the electrolyte was controlled with EG&G–263A Model potentiostat/galvanostat, the other side faced the air. The Ppy films were potentiostatically deposited at a potential of  $0.7 \text{ V}$  (vs. SCE). The deposition was stopped when the resonance frequency had decreased by ca.  $10 \text{ kHz}$ . The resonance frequency shift caused by the change of mass was measured using a network analyzer (Advantest R3753BH) and transferred to a PC compatible computer. A three-electrode system with the quartz crystal as working electrode, a Pt gauze counter electrode and the saturated calomel reference electrode (SCE) was employed.

Scanning electron microscopy (SEM) investigations were performed with a Zeiss DSM 982 Gemini microscope (Carl Zeiss, Germany).

## 3. Results and discussion

### 3.1. Film synthesis and morphology

Figure 1 shows a typical potential-time curve obtained during the galvanic deposition of Ppy doped with molybdate ( $\text{Ppy}(\text{MoO}_4)$ ) on mild steel in one-step procedure.

The polymerization starts at a constant current of  $1.5 \text{ mA cm}^{-2}$  for which the potential increases rapidly and then decreases slowly. After  $100 \text{ s}$ , the potential is stabilised at about  $0.9 \text{ V}$  (vs. SCE) which corresponds to the oxidation potential of pyrrole.

It is worth noting that the polymerisation occurs without an induction period in contrast to other procedures which have been reported [7, 14, 15]. This behaviour indicates that the dissolution of mild steel is prevented.

The oxidation potential of pyrrole is higher than normal in this case. The reasons may be: i) the barrier effect of passive layer of molybdate on surface ii) the conductivity of electrolyte.

The films formed on mild steel are homogenous, compact and conductive. This can be seen from the SEM images in Figure 2. The typical cauliflower structure of Ppy film on mild steel was observed comparable with that on Pt.

### 3.2. Detection of the release of anions during reduction

The protection mechanism involves the formation of an insoluble iron-dopant salt at the metal surface introduced by the reduction of the ICPs galvanically coupled to iron. Kinlen et al. [10, 11] have demonstrated the

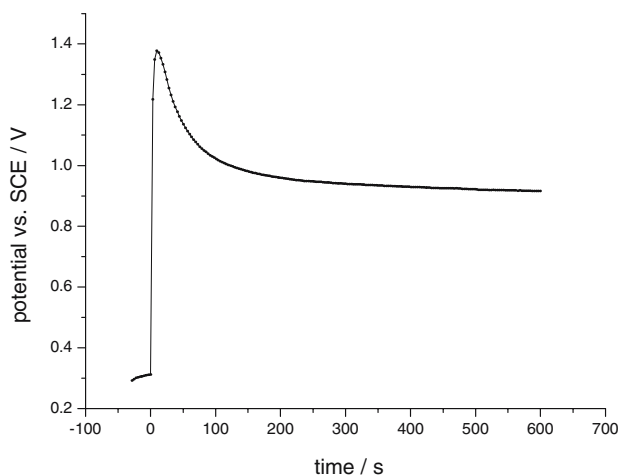


Fig. 1. Potential-time curve for galvanostatic electropolymerisation of Ppy on mild steel in solution of  $0.01 \text{ M}$  molybdate,  $0.1 \text{ M}$  pyrrole,  $\text{pH} = 4.8$ , at  $1.5 \text{ mA cm}^{-2}$ .

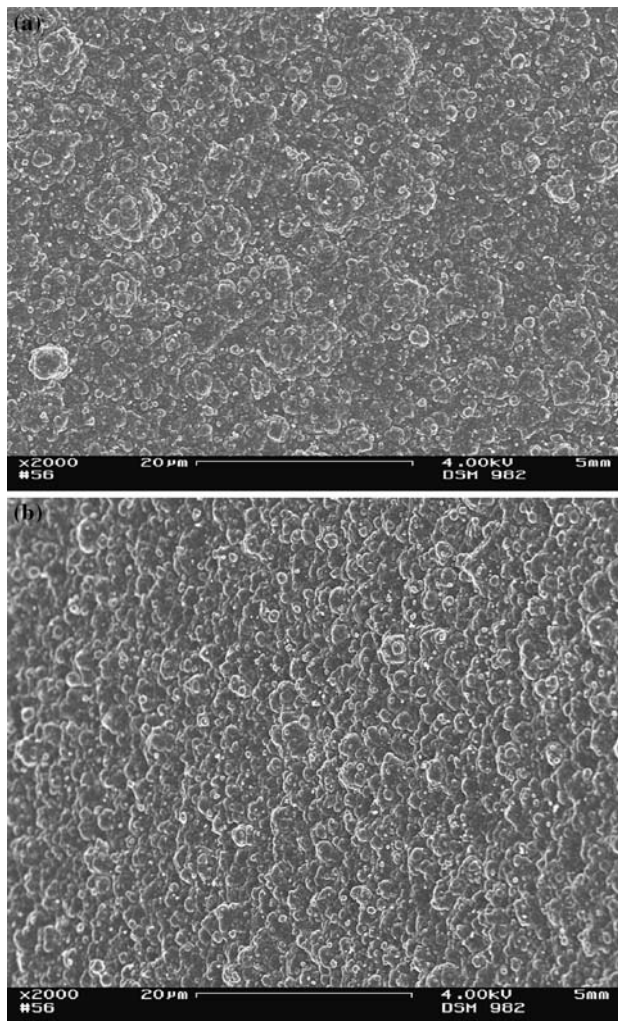


Fig. 2. SEM microphotograph of 1 μm thick Ppy(MoO<sub>4</sub>) film on mild steel (a) and on Pt (b).

corrosion protection by Pani coatings using a scanning reference electrode technique (SRET). The coatings were formulated with different dopant anions and it was found that phosphonic acid dopants give better protection than sulfonic acid dopants. Phosphonate anions can stop the galvanic activity in pinholes in contrast to sulfonate anions which cannot form an iron/dopant complex at the coating/iron interface.

We have investigated the ability of molybdate to enhance the corrosion protection of ICP. If the protective properties of molybdate should be used in ICPs it is necessary that the anion can release from the polymer during reduction in a short time. For investigation of mobility of molybdate Ppy films were studied by EQCM and EIS measurements combined with CV.

Cyclic voltammograms of Ppy(MoO<sub>4</sub>) films grown on Pt are shown in Figure 3. Beginning at 0.6 V (vs. SCE) the Ppy(MoO<sub>4</sub>) film is reduced in tetrabutylammonium bromide (N(Bu)<sub>4</sub>Br). In the presence of this large cation Ppy reduction is only possible, if the molybdate anion can release from the polymer for charge compensation. The cathodic peak at -0.25 V (vs. SCE) in the first scan is associated with molybdate. In the second cycle this

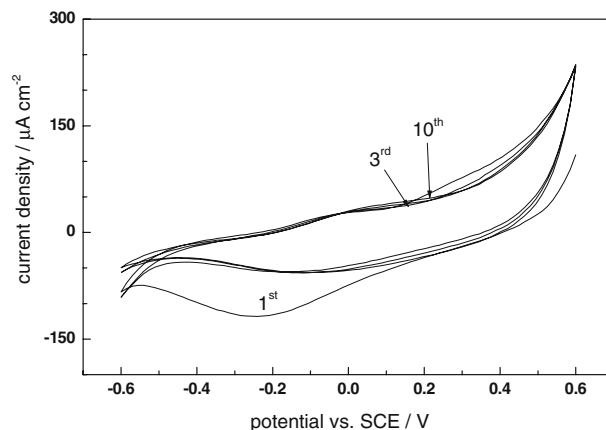


Fig. 3. Cyclic voltammograms of Ppy(MoO<sub>4</sub>) on Pt in 0.1 M N(Bu)<sub>4</sub>Br.

reduction peak is much more smaller and is now associated with the release of bromide. The difference between the reduction peaks in the first and second cycle is generally observed in CVs for redox reactions of ICPs. It is interpreted in the literature as a result of conformation changes of the polymer [18] or of polymer segments of different conjugation length [19]. The presence of the reduction peaks in CVs shows that molybdate anions are mobile enough to release from the polymer film during the cycling process. They are replaced by bromide anions from the supporting electrolyte.

The same behaviour is observed with EIS measurements (Figure 4). The impedance spectra were obtained during the reduction of the polymer in the potential range +0.1 to -1 V (vs. SCE). During reduction the resistance *R* of Ppy increases as marked by the arrow. In the same way, the values of the capacitance decrease indicating that the polymer changes from the conductive state at 0.1 V (vs. SCE) to the semiconducting state at potentials more negative than -0.2 V (vs. SCE). The decrease in

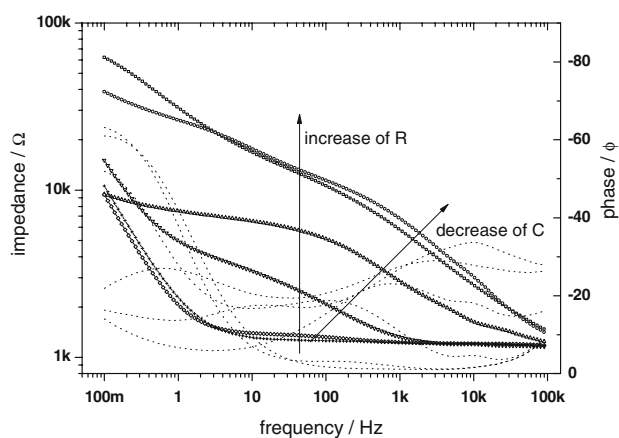


Fig. 4. Bode plots of Ppy(MoO<sub>4</sub>) on Pt reduced at 0.1 V (+); 0 V (◇); -0.4 V (▽); -0.6 V (Δ); -0.8 V (○) and -1 V (□) in 0.1 M N(Bu)<sub>4</sub>Br. The phase angle is indicated by dot lines.

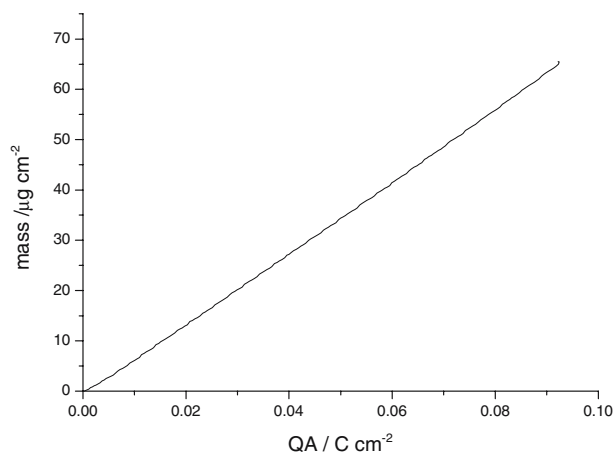


Fig. 5. Mass change vs. passed charge during electrodeposition of Ppy(MoO<sub>4</sub>) on quartz crystal electrode at 0.7 V (vs. SCE); 0.1 M monomer pyrrole, 0.01 M molybdate.

capacitance is only observed if the dopant anion can release from the polymer during reduction. If the anion is too large it remains into the polymer and there is no change in capacitance during reduction as observed with the large size anion polystyrenesulfonate [20].

Figure 5 shows the mass change of the quartz during electropolymerization of pyrrole doped with molybdate. The linearity of frequency shift vs. the passed charge indicates that the Ppy film is homogenous and compact under these conditions.

For the study of the anion exchange, the EQCM technique combined with CV was used. With this method it is possible to study the redox processes of ICPs and to evaluate the charge carrier mobility in doped ICP films [21]. A Ppy(MoO<sub>4</sub>) film synthesised on a quartz electrode was immersed in 0.1 M N(Bu)<sub>4</sub>Br and its mass was controlled during the first cathodic sweep in the range 0.5 to -0.6 V (vs. SCE). The change of polymer mass was calculated with the Sauerbrey equation  $\Delta f = C_{SC} \Delta m$ . The Sauerbrey constant is  $C_{SC} = 226.01 \text{ Hz cm}^2 \mu\text{g}^{-1}$  for a 10 MHz quartz [17, 22].

Typical relation of mass-current response is shown in Figure 6.

It is clear from the mass-potential curve that the mass decreases; molybdate anions release the polymer during reduction. During oxidation the small bromide anion from the solution is incorporated into the polymer film. The mass increases again. The difference in the mass after one cycle derives from the difference in the molar mass of molybdate and bromide. From the ratio of the mass change and the electrical charge passed  $\Delta m/Q$  in Figure 5 the molar mass of molybdate ( $M = 131 \text{ g mol}^{-1}$ ) was calculated [17, 23]. It is compared with the real molar mass in the form MoO<sub>4</sub>  $M = 159.94 \text{ g mol}^{-1}$ . The difference in molar mass may be due to the transport of water taking place in the potential scan [23].

Consequently, the result of the EQCM experiment confirms the mobility of molybdate anion within the polymer film.

### 3.3. Corrosion test

The corrosion behaviour of mild steel covered by Ppy(MoO<sub>4</sub>) films was investigated by OCP-time measurements. The samples were immersed in a 0.1 M NaCl solution as corrosive medium and the OCP was followed vs. time. The protection time is characterized by the time during which the OCP of the covered electrode remains in the passive state of mild steel before it drops to the corrosion potential of unprotected mild steel.

Immersed in 0.1 M NaCl solution, the OCP is initially positive by about 0.35 V (vs. SCE) which corresponds to the potential of the redox process in the Ppy film (Figure 3). The mild steel electrode is maintained in its passive state for about 8 h. Then, the potential sharply decreases to a second plateau at about -0.2 V (vs. SCE). At this stage the chloride ions have reached the mild steel surface and the corrosion starts as anodic reaction. The conducting polymer is reduced partially and mobile molybdate anions release from the polymer. Now the mild steel surface can be passivated by molybdate. The potential of -0.2 V (vs. SCE) corresponds to the

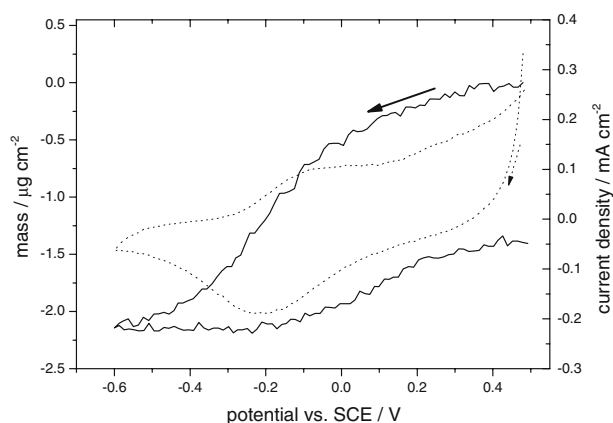


Fig. 6. Cyclic voltammogram (...) and the mass change (—) vs. potential of Ppy(MoO<sub>4</sub>) in 0.1 M tetrabutylammoniumbromide (N(Bu)<sub>4</sub>Br) solution. The scan rate is  $20 \text{ mV s}^{-1}$ .

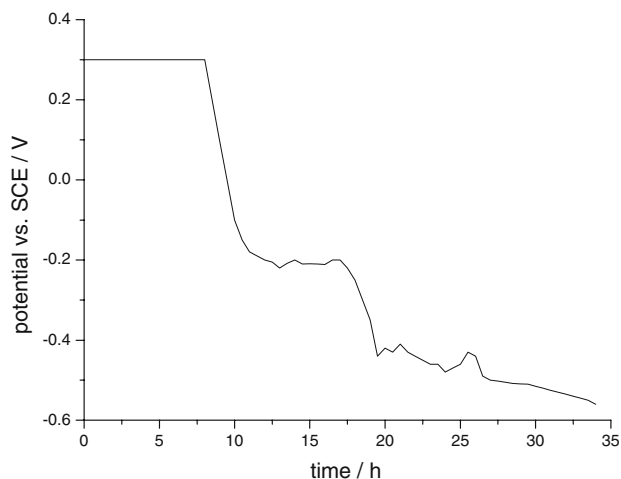


Fig. 7. OCP vs. time curve for mild steel covered with Ppy(MoO<sub>4</sub>) in 0.1 M NaCl.

potential of mild steel immersed in sodium molybdate solution.

This second plateau is only observed if the dopant anion of the conducting polymer has some ability to inhibit the corrosion reaction of mild steel [7, 24]. If the anion cannot give this protection, the second plateau is missing and the potential falls down to the corrosion potential of mild steel at the end of the first plateau [25].

Finally, the OCP decreases toward the corrosion potential of the metal if the concentration of chloride is too large.

The OCP measurements clearly show that the corrosion efficiency of Ppy films can be improved by using molybdate anions as dopant anions.

### 3.4. The self-healing ability of Ppy(MoO<sub>4</sub>) films with small defects

A Ppy film containing molybdate was prepared on mild steel. A small defect (about 0.04 mm<sup>2</sup>) was made on the film using a needle. The sample was immersed in 0.1 M NaCl and the OCP was followed with time (Figure 8a). The OCP remains in the passive range of iron. The potential (about -0.1 V vs. SCE) corresponds to the second plateau in Figure 7. The fluctuations are typical for a permanent passivation process by molybdate and activation process by chloride. In the case of hexafluorophosphate as dopant anion, passivation cannot take place because this anion has no inhibition effect. Immediately after immersion the OCP is in the active range of iron dissolution (Figure 8b). This behaviour shows clearly that Ppy alone is not able to protect mild steel from corrosion.

This result is confirmed by potentiodynamic curves of mild steel with Ppy films with defects (Figure 9).

The corrosion potential of mild steel/Ppy(MoO<sub>4</sub>) is about 0.4 V (vs. SCE) more positive than that of mild

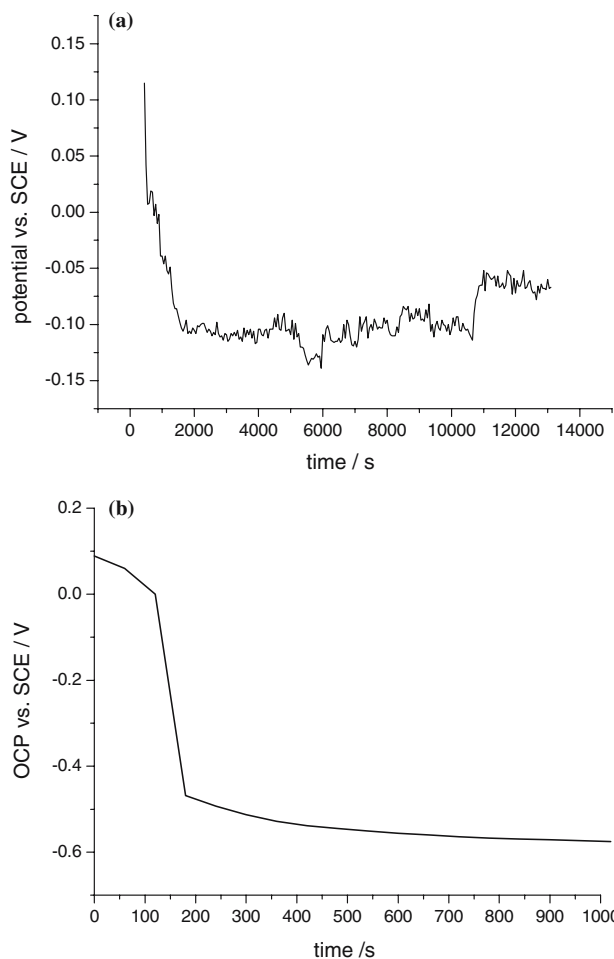


Fig. 8. OCP-time measurements of Ppy film on mild steel with defect a. Ppy(MoO<sub>4</sub>); b. Ppy(PF<sub>6</sub>).

steel/Ppy(PF<sub>6</sub>). With the inhibitor anion molybdate the Ppy film is able to passivate the defect and the corrosion current is 100 times smaller than that of Ppy(PF<sub>6</sub>).

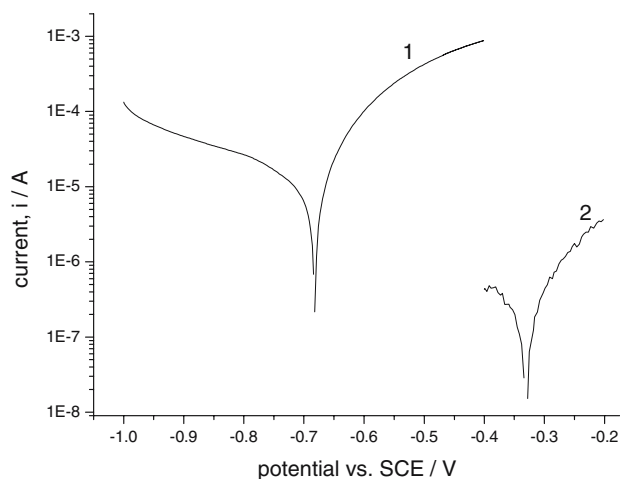


Fig. 9. Potentiodynamic curves of Ppy films with defect in 0.1 M NaCl 1: mild steel/Ppy(PF<sub>6</sub>),  $i_{\text{corr}} = 8 \times 10^{-4}$  A 2: mild steel/Ppy(MoO<sub>4</sub>),  $i_{\text{corr}} = 8 \times 10^{-6}$  A.

#### 4. Conclusions

Ppy films doped with molybdate are able to inhibit mild steel corrosion in a corrosive environment. The Ppy film is galvanically coupled to mild steel. If the corrosion reaction starts at a film defect Ppy is partially reduced thereby releasing the dopant anion molybdate, which then stops the corrosion within the defect. This protection mechanism is possible, since the mobility of molybdate is high enough to migrate through the Ppy film in a short time and form a passive layer on the corroding metal within the defect.

The EQCM and EIS techniques combined with CV were successfully used to study the redox processes taking place in the Ppy film and to control the mobility of molybdate anions.

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