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Citation	Corrosion Science, 49(8), 3442-3452 https://doi.org/10.1016/j.corsci.2007.03.007
Issue Date	2007-08
Doc URL	http://hdl.handle.net/2115/29744
Type	article (author version)
File Information	CS49-8.pdf



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The effect of counter-anions on corrosion resistance of steel
covered by bi-layered polypyrrole film

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Abstract

The bi-layered polypyrrole (PPy) coatings were investigated for corrosion prevention of a carbon steel. The inner layer was doped with the Keggin structure anions of $\text{PMo}_{12}\text{O}_{40}^{3-}$ (PMo_{12}) and HPO_4^{2-} anions for stabilization of the passive oxide film at the metal-polymer interface, and the outer layer was doped with four organic anions of dihydroxynaphthalenedisulfonate (DHNDS), naphthalenedisulfonate (NDS), anthraquinonedisulfonate (AnqDS) or dodecylsulfate (DoS) for inhibition of the decomposition and release of PMo_{12} . The corrosion tests were performed in 3.5 wt.% NaCl aqueous solution. The corrosion resistance of the steels covered by the bi-layered PPy films was found in the following order: PPy- PMo_{12} /PPy-DHNDS < PPy- PMo_{12} /PPy-NDS < PPy- PMo_{12} /AnqDS < PPy- PMo_{12} /PPy-DoS. The performance of corrosion protection related to the oxidized state of the polymer was discussed.

Keywords: A. Polypyrrole; A. Conductive Polymer; B. GD-OES; C. Corrosion Protection;
C. Passivation

1. Introduction

In the last decade the conductive polymers (CP) have been studied by many authors for application to corrosion-resistant coating of metals, because the Cr(VI) was considered as a carcinogen [1,2] and the CP coating has been assumed to be a possible treatment for the replacement of the chromate treatment. Chromate is thought to induce the passivation of metals by its oxidizing property. The CP coatings work as an oxidant to the substrate metals and make a stable oxide film, i.e., passivation film formed on the metals. Among the CP coatings, polyaniline (PANI) [3-5] and polypyrrole (PPy) [6-8] have been widely investigated for corrosion-resistant coatings, because they can be easily formed by electropolymerization in aqueous solutions.

Passivation of steels by CP was firstly reported by DeBerry in 1985 [9]. He reported that stainless steels covered by a thin PANI film were kept at relatively high potential of the passivation in a sulfuric acid solution for long time period, and their corrosion rate was significantly reduced. Wessling deposited a coating containing dispersed PANI on steel without electrochemical treatment and found that PANI dispersed in the coating introduced dissolution of the steel in the initial step and growth of stable oxide film in the following step [10]. These studies indicated that the oxidative CPs induced a stable oxide film formation between the substrate steel and the CP coating, and provided the stable corrosion resistance to the steel. For further enhancement of the resistance, the more stable passivation film is required. For formation of the stable oxide film, we noticed that the counter anions should be doped to the CP during the electropolymerization. We selected for the anion molybdophosphate ion, $\text{PMo}_{12}\text{O}_{40}^{3-}$,

(PMo₁₂) [11-13] which has the Keggin structure and relatively large molecular size. PMo₁₂ can work as an inhibitor facilitating passivation of steels and be strictly fixed in the polymer matrix due to the large molecular size [14,15]. In addition, the PMo₁₂ anion lowered the polymerization potential of PPy formation from pyrrole (Py) monomer probably due to their catalytic property [16].

In the previous paper, we reported that the PPy coating doped with PMo₁₂ (PPy-PMo₁₂ layer) easily induced passivation of the steel and kept the steel in the passive state for 2 days in neutral NaCl solution and for 3 days in acidic NaCl solution [16]. Degradation of the PPy coating, however, took place gradually during the immersion in aqueous solution due to reduction of the PPy matrix with corrosion of Fe to Fe²⁺ or Fe³⁺. During immersion, PMo₁₂ anions undergo hydrolysis with water penetrating in the PPy layer to change to molybdate and phosphate anions. To maintain the neutrality, the reduction of PPy matrix is simultaneously accompanied by release of the molybdate and phosphate anions with relatively small size. Since the passivation of the steel is assumed to be kept by an oxidative action of PPy matrix and by an action of passivator of PMo₁₂, the reduction of the PPy matrix accompanied by the decomposition-release process of PMo₁₂ may induce the de-passivation of the steel. For prolonging the protection duration, the hydrolysis decomposition-release process of the counter anions of PMo₁₂ should be prevented. In our previous paper, an additional PPy over-layer was introduced, which was doped with naphthalenedisulfonate anions (PPy-NDS layer) for preventing the hydrolysis decomposition and release of the counter anions of PMo₁₂ occluded in the inner PPy layer [17]. The introduction of the outer PPy layer doped with

the organic anions prolonged the passive protection time period during corrosion test in an aqueous NaCl solution.

In this paper we prepared on steels bi-layered PPy coatings which consisted of the inner PPy-PMo₁₂ layer and the four different PPy outer layers occluding four organic anions; dihydroxynaphthalenedisulfonate (DHNDS), naphthalenedisulfonate (NDS), anthraquinonedisulfonate (AnqDS), and dodecylsulfate (DoS). The structure of the organic anions used are presented in Fig. 1. The corrosion resistance of the coatings was evaluated in the corrosion test in 3.5 wt.% NaCl solution. The bi-layered coating consisting of the inner PPy-PMo₁₂ and the outer PPy-DoS exhibited the best property of corrosion protection of the steel. We discuss the performance of corrosion protection which may be closely related to the oxidized state of the PPy coatings.

2. Experimental

Pyrrole monomer (Py) purchased from Kanto Chemical Co. (99% purity) was used without any pretreatment. All the other reagents at analytical grade were purchased from Wako Pure Chemical Ltd. Solutions used were prepared from double distilled and subsequently deionized Milli-Q water, and deoxygenated by nitrogen bubbling for 30 min before use. The carbon steel with the composition of C 0.032, Si 0.013, Mn 0.15, P 0.012, S 0.008, Al 0.018 and Fe 99.767 wt. % was mechanically polished with 800-grade abrasive paper and degreased in acetone in ultrasonic bath before use. The geometrical surface of the steel electrodes was about 3 cm².

A three-electrode cell was used for electrodeposition of PPy on the steel substrate. An Ag/AgCl/sat. KCl and a platinum foil were used as a reference and the counter electrodes, respectively. The electrodeposition was carried out at room temperature.

Four types of the bi-layered PPy coatings were prepared on the steel, which consisted of the inner PPy-PMo₁₂ layer and the outer PPy layer doped with one of four organic anions of DHNDS, NDS, AnqDS, and DoS (Fig. 1). Electrosynthesis process was preceded by passivation of steel in 0.06 M disodium molybdate (Na₂MoO₄) solution under potentiostatic condition at 0.8 V for 30 min. After that, the solution was exchanged with solution containing 0.1 M pyrrole (Py) monomer, 0.2 M H₃PO₄, and 5 mM H₃PMo₁₂O₄₀ (H₃PMo₁₂) in which the inner layer of the bi-layered PPy film was formed galvanostatically at a constant current of 1.0 mA cm⁻² for 1000s. The solution was then exchanged with one of the four organic salt solutions: 5 mM 2.7-

dihydroxynaphthalene-3,6-disulfonic acid disodium salt (Na_2DHNDS), 5 mM 1,5-naphthalenedisulfonic acid disodium salt (Na_2NDS), 5 mM anthraquinone-1,5-disulfonic acid disodium salt (Na_2AnqDS), and 25 mM sodium dodecylsulfate (NaDoS). In the solution containing 0.1 M Py monomer, the outer layer of the bi-layered PPy film was formed galvanostatically at a constant current of 1.0 mA cm^{-2} . The total electricity for the formation of the bi-layered PPy film was 2.0 C cm^{-2} .

Thicknesses of the PPy films were measured by the Confocal Laser Scanning Microscopy "Laser-Tech 1LD21D". Evaluation of the thickness was done by measuring the distance difference between coated and uncoated steel surfaces.

Depth profile of elements in the PPy films was measured by the Glow Discharge Optical Emission Microscopy (GD-OES) "JY-5000 RF" with sampling diameter of 5mm.

The electric resistance of the coatings was evaluated by measuring the impedance of the coated steel pressed by two gold plates from the both sides. The geometrical area of the gold plate was 0.785 cm^2 . The NF Electronic Instruments 5020 Frequency Response Analyzer was used for the impedance measurements. The measurement was performed in the frequency range from 20 kHz to 10 mHz.

The corrosion tests of the PPy coated steel were carried out at $25.0 \pm 0.3 \text{ }^\circ\text{C}$ in the 3.5 wt.% NaCl solution in which the open circuit potential (OCP) was continuously recorded for 7 or more days.

3. Results

3.1 Thickness, density and conductivity of PPy films

The thickness evaluated by CLSM and the density evaluated from the ratio of the mass to the thickness are summarized in Table 1. The densities of PPy layers reveal large difference, depending on doped anions. The lowest density is seen for the PPy layers doped with NDS and AnqDS. The density of the PPy layer doped with DoS anions is 3.6 g cm^{-3} close to that of the layer doped with inorganic anions of PMo_{12} . It is assumed that cross-linking takes place between a linear chain of DoS and PPy backbone, resulting in the high density of the PPy-DoS film. The highest density of 4.3 g cm^{-3} is found for the polymer doped with DHNDS. Such a dense film may result from a very low concentration of dopant in PPy matrix. The similar dense film was formed when PPy was electrodeposited from Py monomer in pure water without any supporting solution [17]. Su and Iroh also reported a less porous and more dense structure of PPy film, when the concentration of dopant in electrolyte was extremely low [18].

The electric resistance of the coatings was evaluated by measuring AC impedance of the coated steel samples covered by the bi-layered PPy. The impedance was measured between two gold electrodes pressed to both sides of the coated steel. Although the measured impedance is supposed to include the PPy film and the thin passive oxide film at the metal-PPy interface, they are not distinguishable from each other on the impedance-frequency diagram. The electric resistance and the conductivity calculated of the coatings are summarized in Table 2. The conductivity of the coating

ranges between $1 \times 10^{-4} \text{ S cm}^{-1}$ and $5 \times 10^{-4} \text{ S cm}^{-1}$. The higher conductivity may be explained by a larger number of cations and radicals fixed to the polymer chain and be associated with the larger doping ratio of counter anions. The lowest conductivity of $1 \times 10^{-4} \text{ S cm}^{-1}$ is evaluated for PPy doped with DHNDS. The conductivity of the bi-layered PPy coatings except for the PPy-PMo₁₂/PPy-DHNDS is higher than that of the inner PPy-PMo₁₂ layer measured before deposition of the outer PPy layer. We suppose that during the second step of electropolymerization, the re-oxidation of polymer chain in the inner layer takes place and simultaneously the organic counter-anions are incorporated into the inner layer. This means that the inner PPy layer is changed to that doped with both inorganic and organic anions. Relatively high conductivity of the PPy-PMo₁₂/PPy-DoS film may indicate that the doping ratio of DoS anions is much higher than that of the other dopants.

3.2 Morphology and depth profile

The surface morphology of the bi-layered PPy films doped with the different organic counter anions is shown in Fig. 2. Figures 2b and 2c show the SEM views of the PPy layers doped with NDS and AnqDS, respectively, in which globular morphology with variable particle size from 2 to 10 μm diameter is observed. The surface of PPy doped with DHNDS (Fig. 2d) is characterized by a cauliflower-like structure with small grains of 0.5 μm diameter. This type of structure was observed in the case that dopants were not able to easily intercalate into the polymer chain and assumed to be a low concentration of doped counter anions [19]. Another morphology is observed for PPy doped with DoS

(Fig. 2a), in which needle-like flakes of approximately 1 μm length with irregular orientation appear on the globules.

Figure 3 shows the GD-OES depth profiles evaluated for the bi-layered PPy coatings with the outer layer doped with DoS, NDS, AnqDS, or DHNDS. Three regions corresponding to the outer layer, inner layer, and steel substrate are distinguishable on the profiles. Similar distribution of P and Mo appears in the inner layer of the four bi-layered coatings. From the intensity of S detected in the outer layer, the doping ratio of sulfate or sulfonates incorporated into PPy matrix can be estimated. Since re-oxidation of the inner PPy part takes place during the second step of electrodeposition, the signal of S is also detected in the inner layer region. In Fig. 3 the boundaries between the outer and inner layers and between the inner layer and steel substrate are not clearly seen probably due to non-uniform sputtering or rough polymer surface. For quantitative analysis of the doping ratio, x , the calibrated intensities of S and C are required. The calibration was made from the GD-OES signals of thin layers of NDS, AnqDS, DHNDS and DoS precipitated on glassy carbon plates from the aqueous solutions. From the ratio of the calibrated intensity of S to C, a molecular number of the doped anions per Py unit, which is defined by a doping level, x , was calculated. The result thus calculated is given in Table 3, in which the doping level is seen in the following order: DoS>AnqDS>NDS>DHNDS. The highest doping level is found to be 0.26 ± 0.039 for the PPy doped with DoS. This value indicates that a DoS ion is doped for every 3.8 Py units as the counter anion.

The conductivity of the PPy coatings may be strictly related to the positive charge density fixed on the PPy matrix. The positive charge number per one Py unit, y , was estimated from the doping level and the valency of the corresponding anions. The charge number is listed on the last column in Table 3. The relation between the charge number and the conductivity is given in Fig. 4. The conductivity is seen to reveal almost linear relationship with the positive charge number except for the coating doped with AnqDS, in which the charge number is higher than that of PPy-NDS, though the conductivity is lower. The positive charge on the PPy backbone may be partially transferred to the redox between quinone and hydroquinone in AnqDS [20,21] and thus the effective positive charge on the PPy backbone may become lower.

3.3 Corrosion tests

The effect of organic counter-anions doped into the outer PPy layer on the corrosion resistance of the coated steels was examined from corrosion test in 3.5 wt.% NaCl aqueous solution, where the open circuit potential (OCP) was measured. Figure 5 shows the OCP of the steels covered by the four bi-layered PPy coatings electrodeposited with electricity of 2 C cm^{-2} . Initially, steels coated by the bi-layered coatings exhibit the open circuit potential of about 0.2 V. After several hours of the immersion, the OCP showed steady values at 0.125 V, 0.138 V, 0.160 V and 0.175 V for steels covered by PPy-PMo₁₂/PPy-DHNDS, PPy-PMo₁₂/PPy-AnqDS, PPy-PMo₁₂/NDS and PPy-PMo₁₂/PPy-DoS, respectively. The initial decrease of potential is associated with the dedoping process of counter-anions, probably of small size anions of HPO₄²⁻, from the inner layer in which both PMo₁₂O₄₀³⁻ and HPO₄²⁻ are doped with the ratio of 1.0 (PMo₁₂O₄₀³⁻) to 2.2 (HPO₄²⁻) [17]. The initial release causes the small loss of the oxidizing power of conductive polymer. The small difference in the steady potentials among the coated steels may be explained by the difference in the oxidized state of the PPy backbone represented by the charge number per one Py unit, as shown in Table 3.

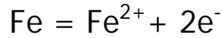
The passive state is maintained for 32 h, 42 h, 100 h and 170 h for the steels covered by PPy-PMo₁₂/PPy-DHNDS, PPy-PMo₁₂/PPy-NDS, PPy-PMo₁₂/AnqDS and PPy-PMo₁₂/PPy-DoS, respectively. The shortest protection duration is seen for the steel coated by PPy-PMo₁₂/PPy-DHNDS and is about 32 h which is the same as that of the steel coated by single PPy-PMo₁₂ film [17]. This means that the protection of steel is

mainly determined by the inner PPy-PMo₁₂ layer and the outer layer of PPy-DHNDS is not effective for the protection of steel.

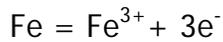
The bi-layered coating of PPy-PMo₁₂/PPy-NDS shows better performance than the PPy-PMo₁₂/PPy-DHNDS coating. The longer protection is probably ascribed to the higher oxidized state of PPy coating. Further improvement of steel protection is found for the steel covered by the bi-layers of PPy-PMo₁₂/PPy-AnqDS and PPy-PMo₁₂/PPy-DoS. The protection time of the PPy-PMo₁₂/PPy-DoS coating is 5 times as long as that of the single PPy-PMo₁₂ coating.

4. Discussion

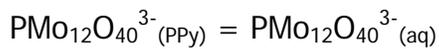
The following mechanism for the degradation process of the single-layer PPy coatings doped with PMo_{12} has been proposed [16]. During immersion of the coated steels in the NaCl solution, oxidation of Fe to Fe^{2+} or Fe^{3+} takes place.



or



The oxidation to Fe^{2+} or Fe^{3+} is accompanied by the reduction of PPy and the release of the counter anions from the PPy layer.



Since penetration of electrolyte into the PPy film gradually takes place, $\text{PMo}_{12}\text{O}_{40}^{3-}$ is decomposed to MoO_4^{2-} and HPO_4^{-} by hydrolysis with the penetrating water.



The molybdate and phosphate anions decomposed are released more easily from PPy coating. After the degradation of the PPy coating, the steel was depassivated and transferred to the active state.

For the further improvement of the corrosion prevention, we introduced the bi-layered PPy film in the previous paper [17]. In the model for the corrosion protection by the bi-layered PPy film, the corrosion protection of steel was proposed to result from the following two factors: i) the stabilization of the passive oxide film by PMo_{12} doped in

the inner layer, and ii) the inhibition of the decomposition-release process of PMo_{12} by the outer layer doped with large size organic ions. In Fig. 5, the bi-layered PPy films were found to be effective for enhancement of the protection performance and the bi-layered PPy doped with DoS in the outer layer was most effective for corrosion prevention of a carbon steel. The effective protection can be suggested to be relate to the oxidized state and density of the PPy coating. As shown in Table 1, the density of PPy film doped with DoS is $\rho=3.6 \text{ g cm}^{-3}$ which is larger than PPy-NDS and PPy-AnqDS, except for PPy-DHNDS which had a highest density, however, it consisted of the PPy layer with a very low doping ratio.

In the following we discuss relation between oxidized state of PPy and the protection of corrosion of the steel. In Fig. 6 the protection time is plotted for individual PPy films as a function of the oxidized state of PPy, y . The oxidized state may be related to the conductivity. In Fig. 7 the protection time is plotted as a function of conductivity. It may be concluded that the PPy coating doped with DoS is most effective for the corrosion prevention because of its highly oxidized state in addition to the enough large density.

Re-oxidation and recovery of the reduced PPy by atmospheric oxygen was proposed by Kinlen et. al [4] and further by other authors [22-24]. If the recovery or re-oxidation of the reduced PPy coating could take place by the reaction with oxygen, the degradation would be delayed. Although the high conductivity may be expected to be related to the higher rate of oxygen reduction, the recovery of the PPy will be examined further.

The prevention of the localized corrosion such as pitting corrosion is one of the important issues. The prevention of aggressive anions such as chloride ions is greatly affected by ionic perm-selectivity of the over-layer on passivated steel. The nature of the counter anion doped in the outer PPy layer and its doping level may have an effect on the ionic perm-selectivity of the polymer film. The ionic perm-selectivity of the bi-layered films is thus under study by using Electrochemical Quartz Crystal Microbalance technique.

5. Conclusions

The bi-layered polypyrrole (PPy) coatings were prepared on steels. The inner layer was doped with $\text{PMo}_{12}\text{O}_{40}^{3-}$ (PMo_{12}) and HPO_4^{2-} for stabilization of the passive oxide film at the steel-polymer interface and the outer layer was doped with organic anions of dihydroxynaphthalenedisulfonate (DHNDS), naphthalenedisulfonate (NDS), anthraquinonedisulfonate (AnqDS) or dodecylsulfate (DoS) for inhibition of the decomposition and release of PMo_{12} .

The bi-layered film doped with PMo_{12} anion in the inner layer and DoS anion doped in the outer layer was most effective for corrosion prevention of steel. The 4.2 μm thick bi-layered PPy film kept the steel in the passive domain for 7 days in 3.5 wt.% NaCl aqueous solution. The corrosion resistance was found to originate in highly oxidized state and large density of the PPy coating doped with DoS counter anion.

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Table captions

Tab 1. Ratio of thickness to electricity, d/Q , for polymerization and density, ρ , of the PPy layers.

Tab 2. The contact resistance of Fe/ox/PPy/Au system and conductivity, σ , calculated for the PPy films.

Tab 3. Doping level, x , for the outer PPy films calculated from the ratio of S and C in GD-OES depth profiles.

Figure captions

Fig. 1. Structures of organic anions used for doping of outer PPy layer: a) dodecylsulfate (DoS), b) dihydroxynaphthalenedisulfonate (DHNDS), c) naphthalenedisulfonate (NDS), d) anthraquinonedisulfonate (AnqDS).

Fig. 2. SEM micrographs of outer PPy layer doped with a) DoS, b) NDS, c) AnqDS and d) DHNDS anions electrodeposited with electricity of 1 C cm^{-2} .

Fig. 3. GD-OES depth profiles of the bi-layered PPy films on steels. The inner PPy layer was prepared in $\text{H}_3\text{PMo}_{12}\text{O}_{40} + \text{H}_3\text{PO}_4 + \text{Py}$ solution with electricity of 1 C cm^{-2} and the outer layer in a) $\text{NaDoS} + \text{Py}$, b) $\text{Na}_2\text{NDS} + \text{Py}$, c) $\text{Na}_2\text{AnqDS} + \text{Py}$ and d) $\text{NaDHNDS} + \text{Py}$ solution with 1 C cm^{-2} .

Fig. 4. The relationship between the ratio of valency per Py unit and the conductivity of the PPy coating doped with four organic anions.

Fig. 5. Open circuit potential as a function of immersion time in 3.5 wt.% NaCl aqueous solution for steel covered by bi-layered (Δ) PPy- PMo_{12} /PPy-DHNDS, (\diamond) PPy- PMo_{12} /PPy-NDS, (\circ) PPy- PMo_{12} /AnqDS, (\square) PPy- PMo_{12} /PPy-DoS coatings electrodeposited with electricity of 2 C cm^{-2} .

Fig. 6. The protection time as a function of the ratio of valency per a Py unit of the PPy coatings doped with four organic anions.

Fig. 7. The relationship between protection time and conductivity of PPy films.

Tab 1. Ratio of thickness to electricity, d/Q , for polymerization and density, ρ , of the PPy layers.

PPy film	d/Q ($\mu\text{m cm}^2/\text{C}$)	ρ (g/cm^3)
PPy-PMo ₁₂	2.1	3.4
PPy-DoS	2.1	3.6
PPy-NDS	2.7	2.1
PPy-AnqDS	2.4	2.2
PPy-DHNDS	1.2	4.3

Tab 2. The contact resistance of Fe/PPy/Au system and conductivity, σ , calculated for the PPy films.

PPy film	Q (C cm ⁻²)	R (Ω cm ²)	σ (S cm ⁻¹)
PPy-PMo ₁₂	1.0	2.0	1.1*10 ⁻⁴
PPy-PMo ₁₂ /PPy-DoS	2.0	0.8	5.2*10 ⁻⁴
PPy-PMo ₁₂ /PPy-NDS	2.0	1.8	2.7*10 ⁻⁴
PPy-PMo ₁₂ /PPy-AnqDS	2.0	2.2	2.0*10 ⁻⁴
PPy-PMo ₁₂ /PPy-DHNDS	2.0	3.3	9.9*10 ⁻⁵

Tab 3. Doping level, x , for the outer PPy films calculated from the ratio of S and C in GD-OES depth profiles.

Doping anion	Doping level x	Number of Py units per doped anion $1/x$	Ratio of valency of PPy oxidation per Py unit y
Dos	0.26 ± 0.039	3.8	0.26
NDS	0.089 ± 0.010	11	0.18
AnqDS	0.12 ± 0.011	8.3	0.23
DHNDS	0.051 ± 0.021	20	0.10

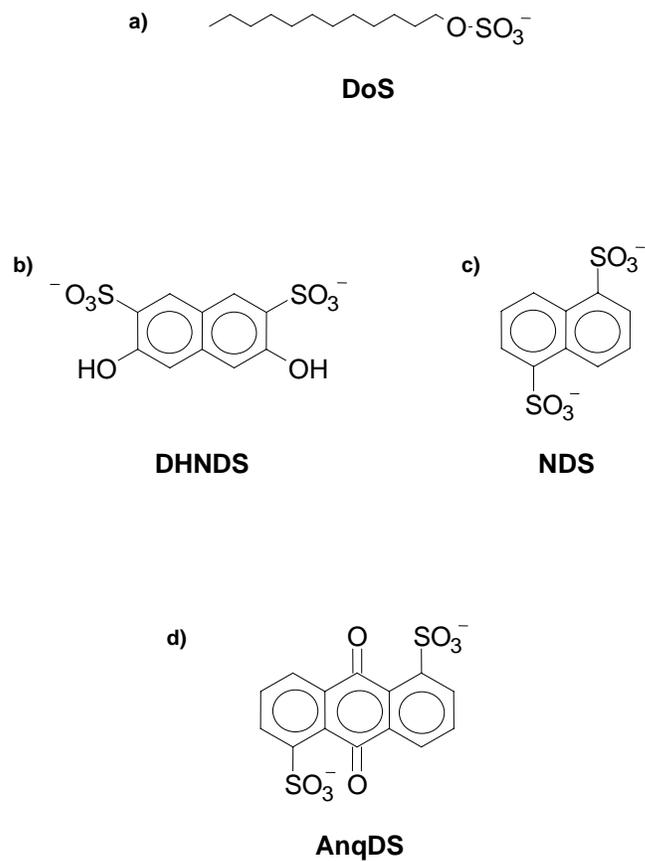


Fig. 1. Structures of organic anions used for doping of outer PPy layer: a) dodecylsulfate (DoS), b) dihydroxynaphthalenedisulfonate (DHNDS), c) naphthalenedisulfonate (NDS), d) anthraquinonedisulfonate (AnqDS).

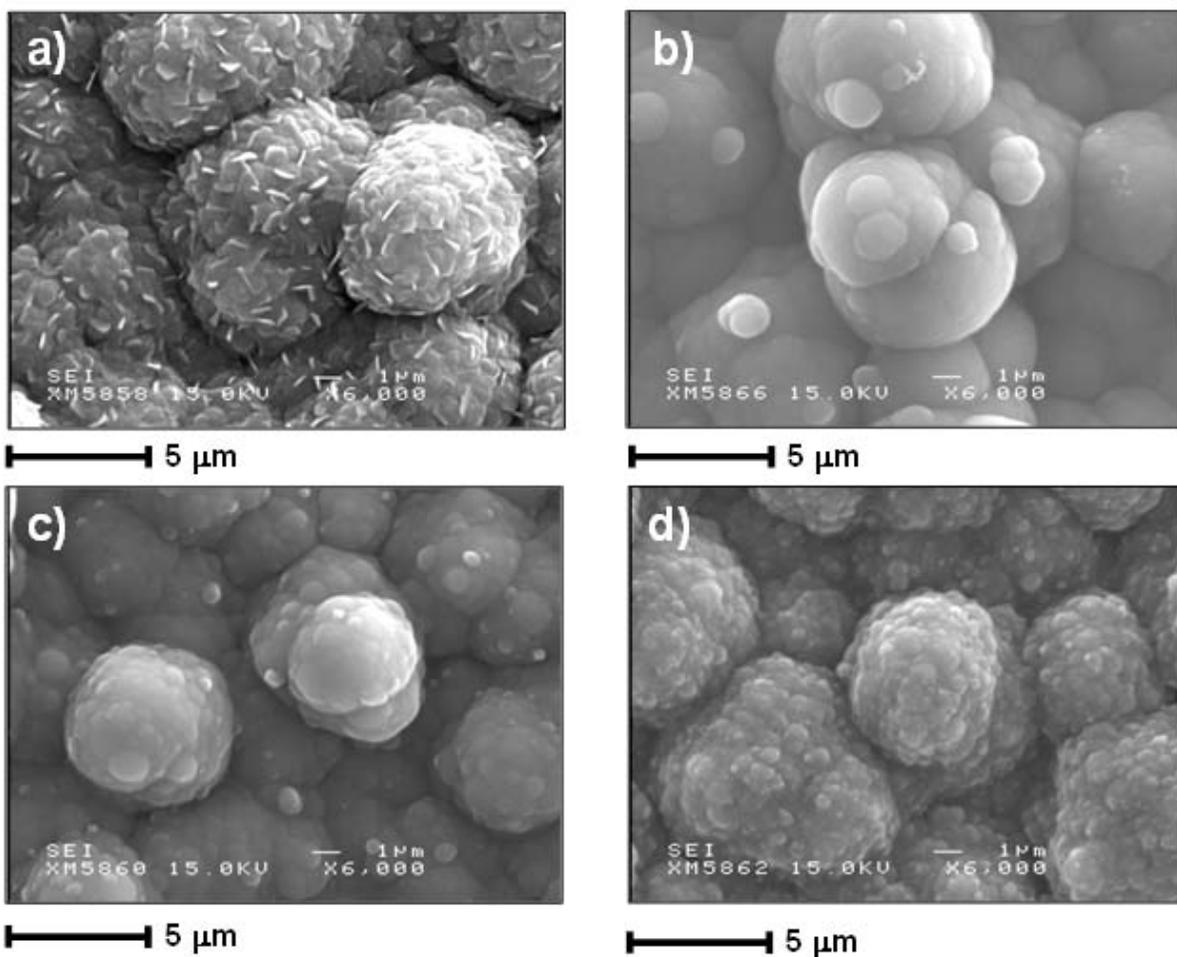


Fig. 2. SEM micrographs of outer PPy layer doped with a) DoS, b) NDS, c) AnQDS and d) DHNDS anions electrodeposited with electricity of 1 C cm^{-2} .

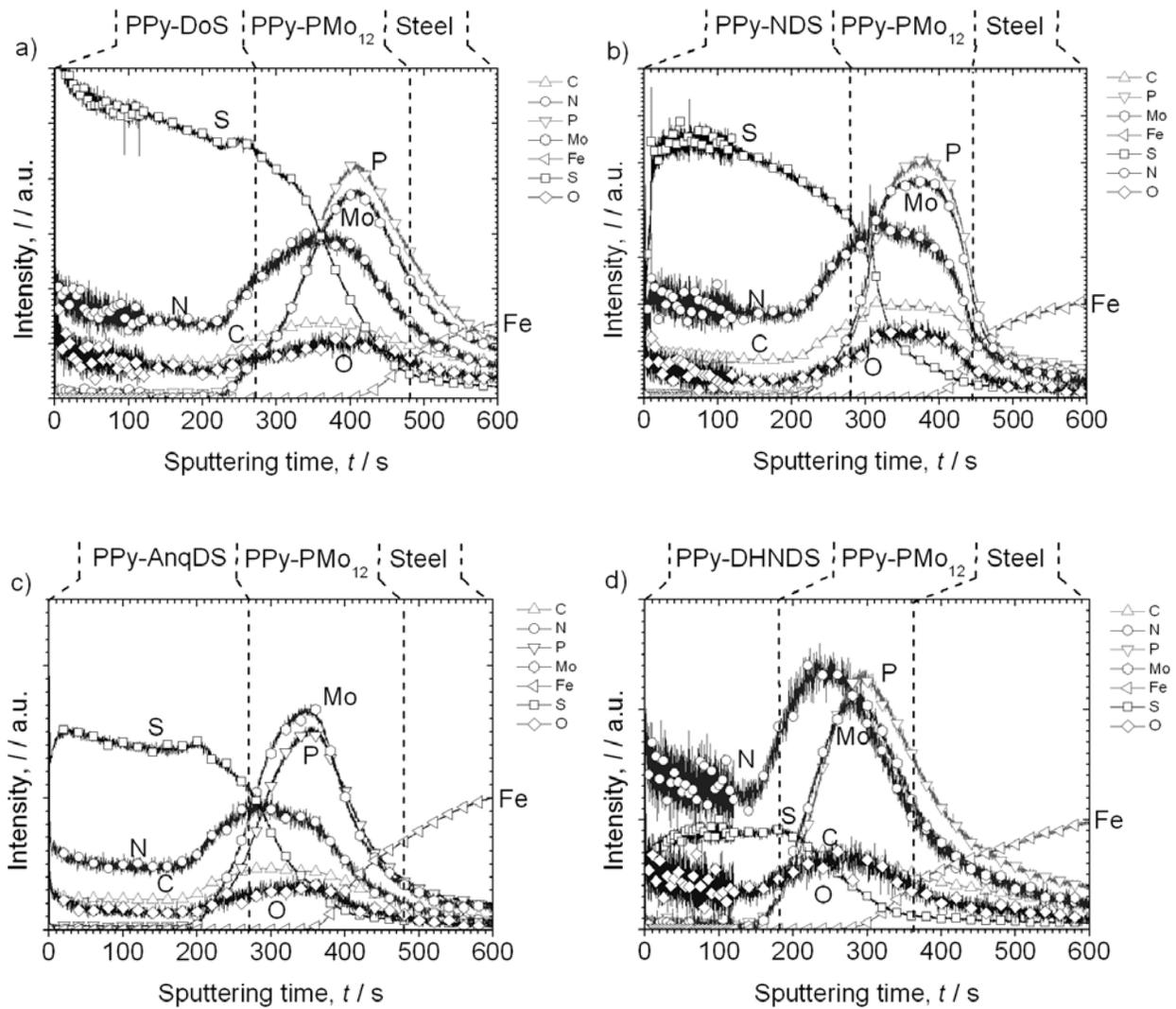


Fig. 3. GD-OES depth profiles of the bi-layered PPy films on steels. The inner PPy layer was prepared in $\text{H}_3\text{PMo}_{12}\text{O}_{40} + \text{H}_3\text{PO}_4 + \text{Py}$ solution with electricity of 1 C cm^{-2} and the outer layer in a) $\text{NaDoS} + \text{Py}$, b) $\text{Na}_2\text{NDS} + \text{Py}$, c) $\text{Na}_2\text{AnqDS} + \text{Py}$ and d) $\text{NaDHNDS} + \text{Py}$ solution with 1 C cm^{-2} .

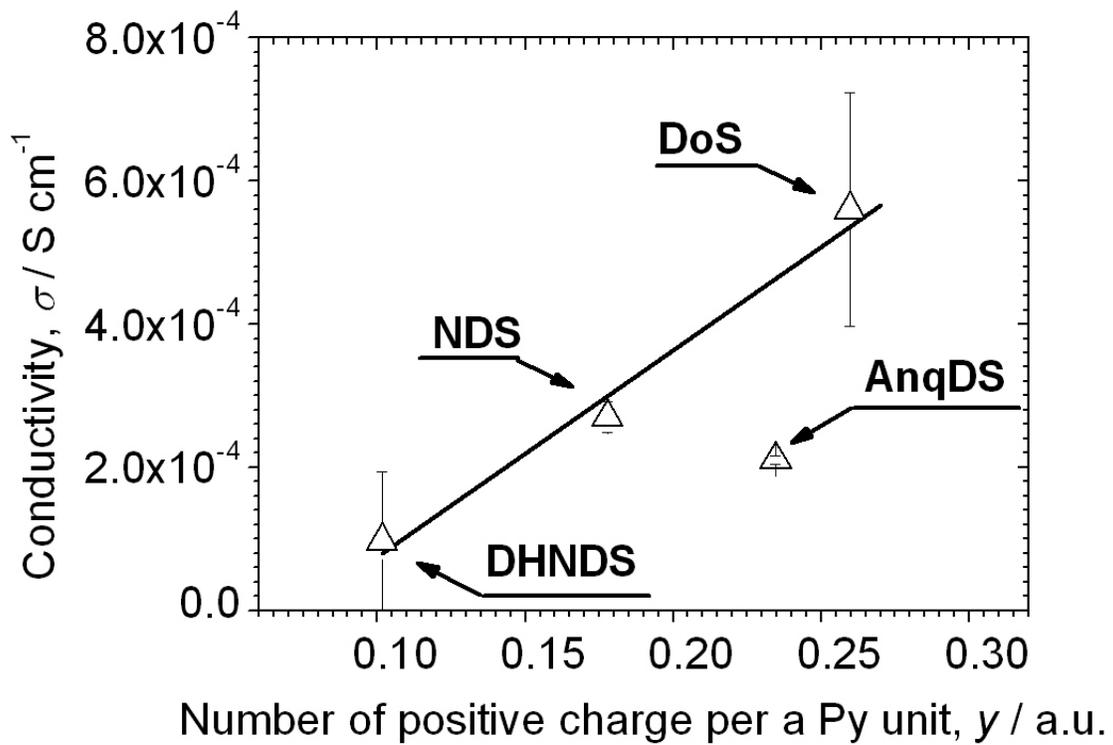


Fig. 4. The relationship between the ratio of valency per Py unit and the conductivity of the PPy coating doped with four organic anions.

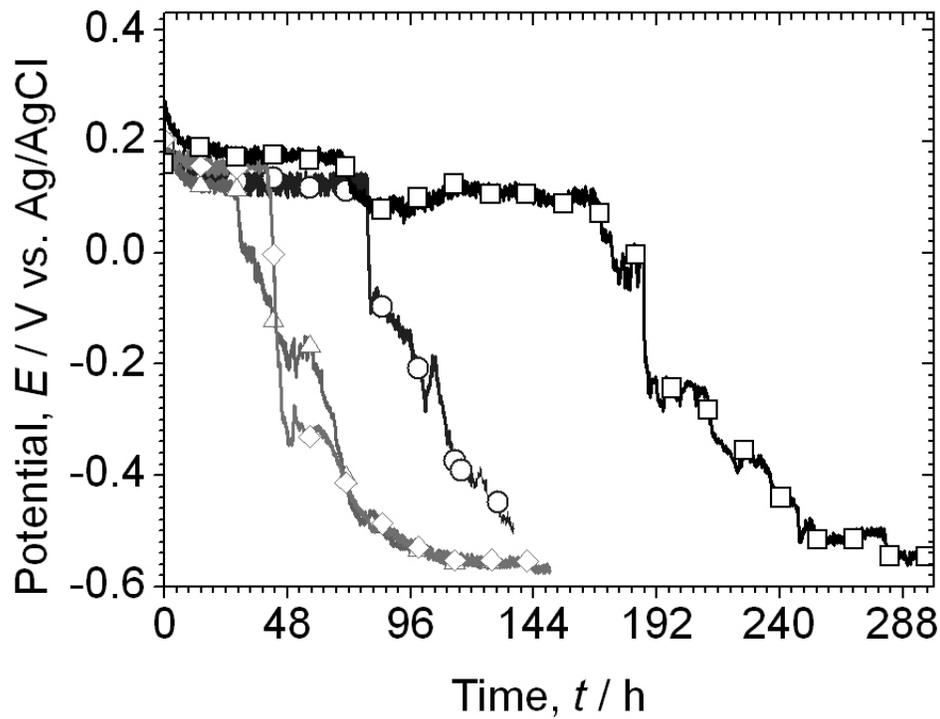


Fig. 5. Open circuit potential as a function of immersion time in 3.5 wt.% NaCl aqueous solution for steel covered by bi-layered (Δ) PPy-PMo₁₂/PPy-DHNDS, (\diamond) PPy-PMo₁₂/PPy-NDS, (O) PPy-PMo₁₂/AnqDS, (\square) PPy-PMo₁₂/PPy-DoS coatings electrodeposited with electricity of 2 C cm⁻².

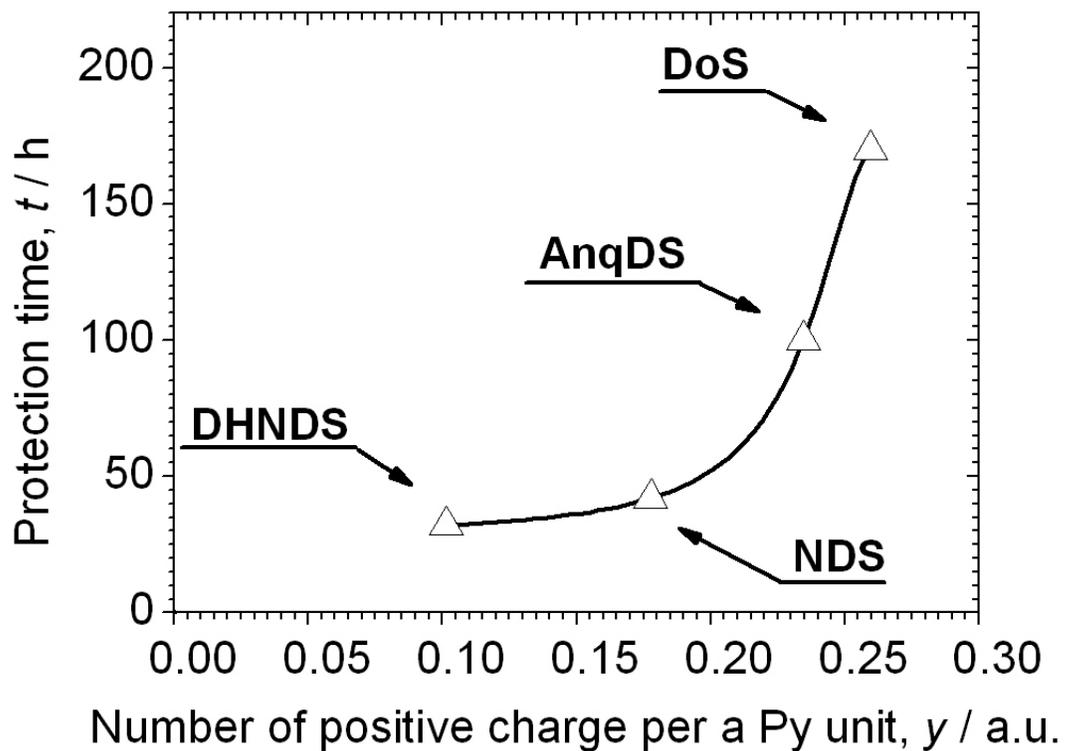


Fig. 6. The protection time as a function of the ratio of valency per a Py unit of the PPy coatings doped with four organic anions.

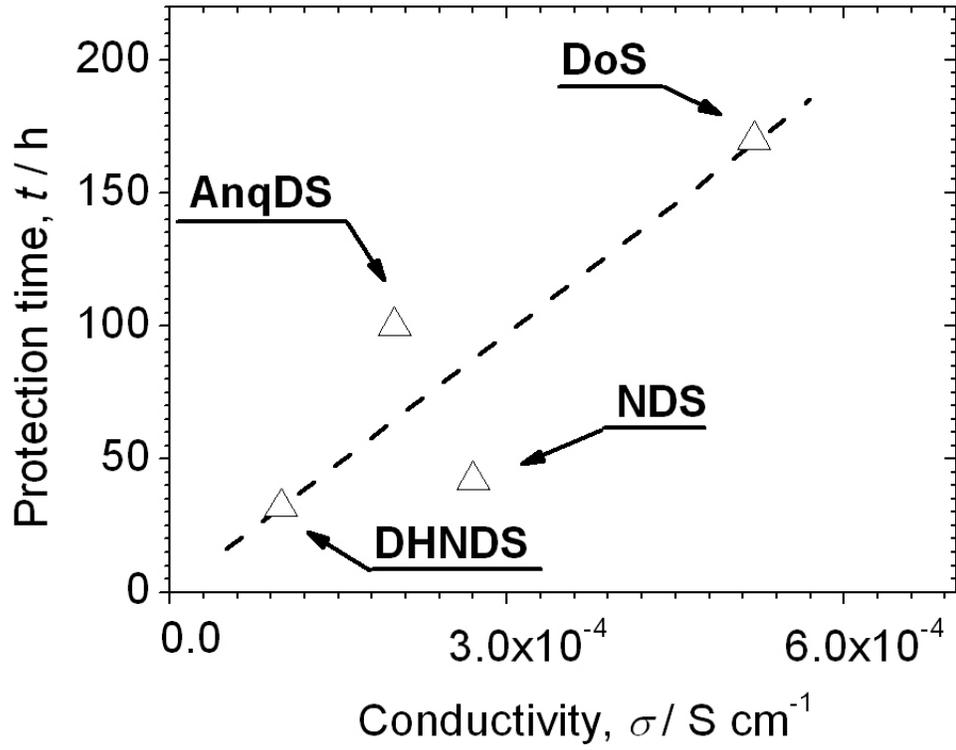


Fig. 7. The relationship between protection time and conductivity of PPy films.