

Toshiaki Ohtsuka · Masahide Iida · Mikito Ueda

Polypyrrole coating doped by molybdo-phosphate anions for corrosion prevention of carbon steels

Received: 24 May 2005 / Accepted: 9 November 2005 / Published online: 13 May 2006
© Springer-Verlag 2006

Abstract The polypyrrole coating was prepared from phosphoric acid aqueous solution containing the heteropolyanion $\text{PMo}_{12}\text{O}_{40}^{3-}$ and pyrrole monomer to make new coating for corrosion prevention of carbon steels. The coating thus formed in the phosphate acid solution was doped by $\text{PMo}_{12}\text{O}_{40}^{3-}$ and by PO_4^{3-} . The coating was flexible enough to cover the steel homogeneously without cracks, although many cracks were observed on the coating formed in a neutral aqueous solution of Na_2MoO_2 . The 5.1- μm -thick polypyrrole coating makes the steel maintain the passive state for 48 h in neutral 3.5 wt% NaCl solution at pH 5.3 and for 80 h in acidic 3.5 wt% NaCl solution at pH 1.9. The coating decreased the corrosion rate of the steel by 1/200 in the neutral NaCl solution and by 1/340 in the acidic NaCl solution, if compared with the rate of the bare steel. The dissolution current of the steel during the immersion remained at the level of the typical passive current in the respective solutions.

Keywords Polypyrrole · Steel · Corrosion prevention · Molybdo-phosphate

Introduction

Many papers have recently been published for corrosion prevention of metals by use of conducting polymer coatings, in which oxidative conducting polymers such as polyaniline (PANI) and polypyrrole (PPy) facilitate formation of passive oxide films on the substrate metals and maintain the passive state of the metals for a long time period. DeBerry was the first to point out the possibility of the conducting polymer coating to protect metals against

corrosion [1]. He reported that stainless steel covered by PANI layer was kept passive state in sulfuric acid solution for a long time period and the corrosion of the stainless steel was greatly prevented in acidic aqueous solution. Other authors also presented the corrosion prevention of stainless steel by PANI coating [2–4] as well as by PPy coating [5, 6]. As the conducting polymer coatings could electrochemically be formed on various metals [7, 8], they were applied to corrosion prevention of various metals of Cu [9], Zn [10], Al [11], Ti [12], CuNi [13], etc.

Many authors have further reported corrosion prevention of carbon steels by conducting polymers. Wessling presented that the carbon steel covered by PANI coating exhibited corrosion potential in the passive-state region and, if pinholes emerged in the PANI coating, the passive state was maintained on the substrate part underneath the pinholes due to a catalytic effect on oxygen reduction reaction of the PANI coating [14, 15]. PPy is also one of the conducting polymers and is easily synthesized by electrochemically anodic oxidation in aqueous and nonaqueous solution [16–22]. Adherence and corrosion prevention of the PPy coatings to steels may greatly depend on the dopant anions which are incorporated as counter-charge particles in the oxidized PPy matrix. Active metals such as steels first undergo active dissolution during the anodic oxidation, followed by coating formation of the polymers. When the dopant anions are not suitable, the electrochemical process does not reach polymer formation but continues the active dissolution of substrate steel. For the formation of the PPy polymer coating on steels, oxalate solutions have been widely used [16–18, 20, 22] because oxalate anions formed with iron cations during the initial active dissolution ferrous oxalate, on which the polymer coating was formed in the second stage. The PPy coating thus formed in oxalate media was reported to reveal good adherence to steels and good prevention against corrosion of steels. As the corrosion prevention of the PPy–oxalate layer thus formed did not, however, continue enough for a long time period, an additional overcoat of PPy doped by organic anions with large size have been introduced on the PPy–oxalate layer, [23–25] or incorporation of oxide

T. Ohtsuka (✉) · M. Iida · M. Ueda
Graduate School of Engineering, Hokkaido University,
Kita 13 Nishi 8, Kita-ku,
Sapporo 060-8628, Japan
e-mail: ohtsuka@elechem1-mc.eng.hokudai.ac.jp
Tel.: +81-11-7066351
Fax: +81-11-7066351

particles or metal particles into the PPy–oxarate layer has been done [26, 27] to enhance the corrosion resistivity.

For establishing high performance against corrosion prevention of steels by PPy, the steel should be stably maintained in the passive potential region and thus covered by the stable passive oxide film. For PPy–oxarate coating, a ferrous oxalate layer relatively thick between the steel substrate and the PPy coating works as the passive layer. In this paper, we prepared a PPy coating doped by hetero-polyanion of $\text{PMo}_{12}\text{O}_{40}^{3-}$ (PPy–MoP coating) and phosphate anions on carbon steels. As the molybdate and phosphate anions doped have been known to work as an accelerator for formation of the passive oxide film, a thin passive oxide film is stably formed on steels underneath the PPy layer and the hetero-polyanion with large size are further firmly fixed as counter-anions in the positively charged PPy matrix. It has been reported that pyrrole was easily polymerized in the presence of hetero-oxometalate poly-anions [28–30] as well as of *iso*-oxometalate poly-anions [31–33]. A corrosion test of the steels covered by the PPy–MoP coating was made in neutral and acidic NaCl aqueous solution to confirm the high corrosion prevention of the PPy–MoP coating.

Experimental

A carbon steel was used, which was obtained from Nippon Steel. The impurities in the steel are following: C 0.032 wt%, Si 0.013 wt%, Mn 0.15 wt%, P 0.012 wt%, S 0.008 wt%, and Al 0.018 wt%. The 0.8-mm-thick steel plate was cut to 30×10 mm, then polished by #800 SiC paper and degreased in acetone in ultrasonic washer.

The pyrrole monomer was purchased from Kanto Chemical (purity 99 %). Other electrolytes were prepared from analytical-grade reagents and Millipore pure water. The electrolytes were deaerated by passing pure nitrogen before use.

The steel plate was firstly passivated at 0.80 V vs Ag/AgCl/Sat. KCl in 0.06 mol dm^{-3} (M) Na_2MoO_4 aqueous solution. After exchange of the solution to a solution containing 0.2 M H_3PO_4 , 5 mM $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, and 0.1, 0.2, or 0.5 M pyrrole (Py) monomer, the PPy coating was formed at a constant current density (CD) of 2.0 or 1.0 mA cm^{-2} with electricity of 2.0 C cm^{-2} .

The steel thus coated by the PPy coating was immersed for 4 days in 3.5 wt% NaCl aqueous solutions at pH 5 and 1.9. The pH of the acidic NaCl solution was controlled by addition of HCl. The immersion area was restricted to $(10 \times 10 \text{ mm}^2) \times 2$ by masking the edge parts with silicon resin. The amounts of Fe ions, Mo ions, and PO_4^{3-} dissolving from the PPy-coated steel into the NaCl solutions were analyzed by inductively coupled plasma atomic emission spectrometry using a Seiko SPS 3000 ICP emission spectrometer.

The thickness of the PPy coating was evaluated from measurement of a distance difference between the coated and uncoated parts by confocal scanning laser microscopy,

Laser-Tech 1LD21D. The surface morphology of the PPy-coated steels was observed by conventional optical microscopy equipped with a CCD camera.

Results

Preparation of PPy–MoP composite coating

Pyrrole monomer was anodically polymerized in aqueous solution of H_3PO_4 – $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ aqueous mixture at constant CD of 1.0 and 2.0 mA cm^{-2} . Figures 1 and 2 show potential-time curves during the anodic polymerization on the steel by 1.0 and 2.0 mA cm^{-2} , respectively, as a parameter of Py monomer concentration. The potential reveals an initial peak and then decreases to potentials in the region from 0.5 to 0.8 V which remain almost constant during the polymerization. The potential in the plateau depends on CD and Py concentration, increasing with the higher CD and the lower concentration of Py. The steel surface was rapidly covered during the anodic polarization by the black PPy film which grew in thickness with time. The initial spike may correspond to nucleus formation of the PPy film and, in the following potential plateau, the PPy film may grow three-dimensionally. The potential during the constant current polymerization is much lower than that previously reported in oxalate solution [16, 17, 19]. The less noble potential may indicate that $\text{PMo}_{12}\text{O}_{40}^{3-}$ anions have a catalytic effect of the polymerization reaction of Py. It was found that $\text{PMo}_{12}\text{O}_{40}^{3-}$ was doped into the PPy coating in addition to PO_4^{3-} from the measurements of the coating surface by X-ray photoemission spectroscopy (XPS) and of depth profile of the coating by glow discharge optical emission spectroscopy (GD-OES), the results of which will be published elsewhere. The presence of $\text{PMo}_{12}\text{O}_{40}^{3-}$ in the PPy coating was also confirmed from the measurement of the anions released from the coating

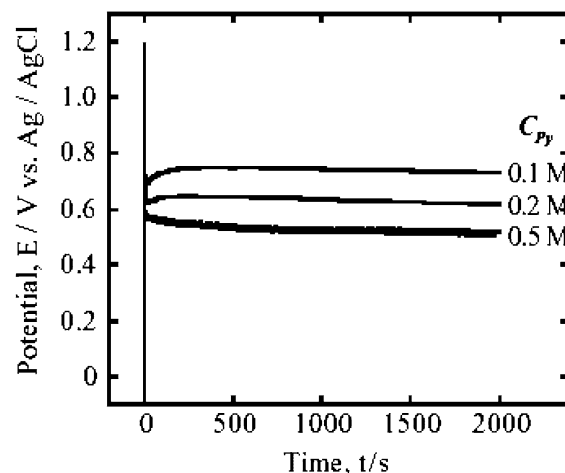


Fig. 1 Potential change with time of the steel during galvanostatic electropolymerization of the PPy–MoP film at 1.0 mA cm^{-2} in 0.2 M phosphoric acid aqueous solution containing pyrrole monomer and 5 mM $\text{PMo}_{12}\text{O}_{40}^{3-}$

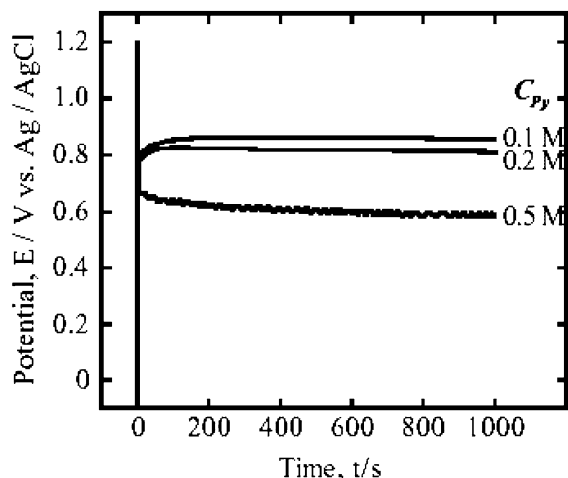


Fig. 2 Potential change with time of the steel during galvanostatic electropolymerization of the PPy–MoP film at 2.0 mA cm^{-2} in 0.2 M phosphoric acid aqueous solution containing pyrrole monomer and $5 \text{ mM PMo}_{12}\text{O}_{40}^{3-}$

into solution during the corrosion test, which will be seen in the following section.

From optical microscopic observation, the PPy film was seen to consist of agglomerates of fine PPy particles. The diameter of the fine particles depended on Py concentration. The diameter was almost homogeneous at $5\text{--}10 \mu\text{m}$ for the film formed at Py concentration of 0.1 M ; however, the film formed at 0.5 M consisted of heterogeneous particles from 5 to $30 \mu\text{m}$ in diameter. The diameter of the fine particles had a tendency to decrease with the smaller CD. For preparation of the denser PPy film consisting of the finer particles, we adopted two-step polymerization in which the polymerization was firstly made by a constant current of 2 mA cm^{-2} for 500 s and secondarily by 1 mA cm^{-2} . In the second step, we believe that the rough coating formed in the first step is filled by fine particles formed by the relatively small CD. Figure 3 shows optical microscopic views of the PPy film surface formed by the two-step polymerization at solution at the Py monomer concentration of 0.1 , 0.2 , and 0.5 M . The surface morphology of the PPy coating formed at 0.1 M Py concentration is seen to be more homogeneous and consists of the finer particles than those formed at 0.2- and 0.5-M concentration of Py monomer.

Thickness and density of the PPy film formed at 2.0 C cm^{-2} electricity are shown in Table 1, where the thickness was evaluated by confocal scanning laser microscopy and the density by comparison between the thickness and weight of the PPy film evaluated from weight difference between before and after the formation of the PPy film. The PPy film formed by the two-step polymerization is seen to be thinner and denser than that by usual one-step polymerization. In the following section on the corrosion test, we used the PPy coating formed by the two-step polymerization in a solution at the Py concentration of 0.1 M .

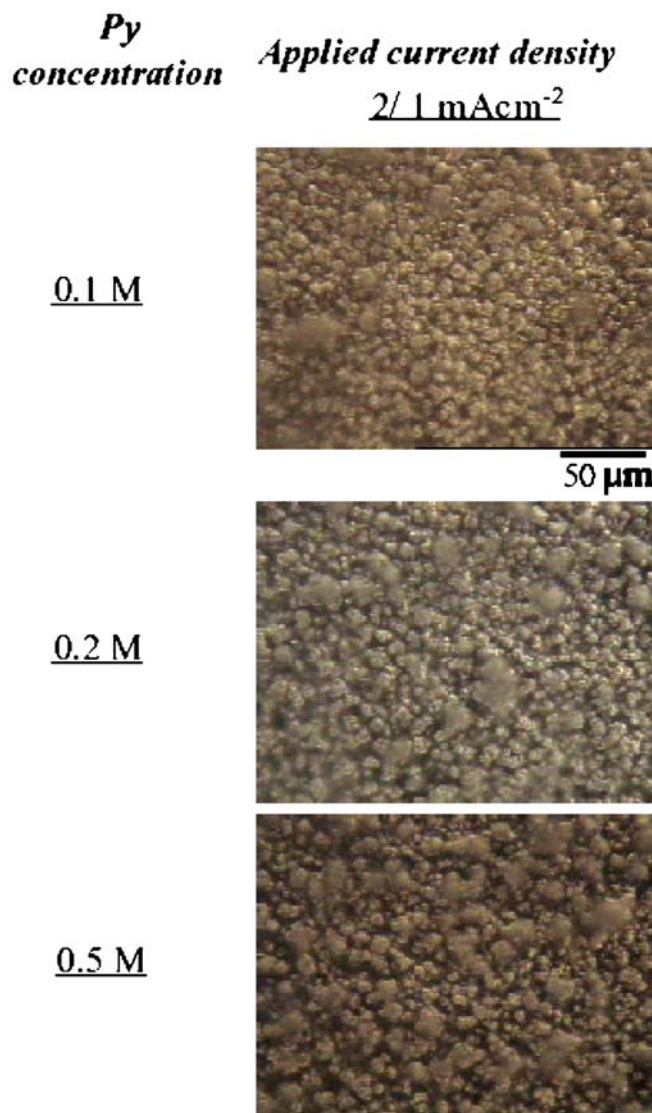


Fig. 3 Optical microscopic view of the surface of the PPy–MoP-coated steel. The coating was prepared by galvanostatic anodic polymerization of 2.0 mA cm^{-2} for 500 s followed by polymerization at 1.0 mA cm^{-2} for $1,000 \text{ s}$

Corrosion test of the steels covered by PPy–MoP coating

Figure 4 shows the corrosion potential of the steel covered with the PPy–MoP coating $5.1\text{-}\mu\text{m}$ thick formed by the

Table 1 Film thickness of and film density of the PPy–MoP coating formed by constant electricity of 2.0 C cm^{-2}

Imposed CD i (mA cm^{-2})	Film thickness i (mm)	Film density ρ (g cm^{-3})
1.0	6.7	2.1
1.0	6.7	2.0
2.0/1.0 ^a	5.1	2.6

^aThe film was formed by two-step polymerization at 2.0 mA cm^{-2} for 500 s and at 1.0 mA cm^{-2} for $1,000 \text{ s}$

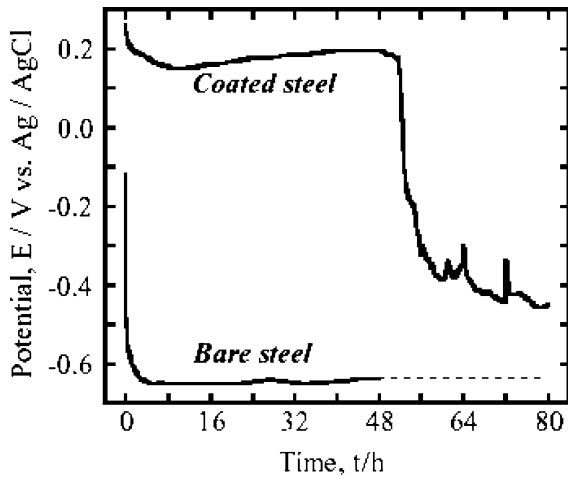


Fig. 4 Change in open circuit potential with time of the PPy-MoP coated steel and the bare steel in neutral 3.5 wt% NaCl solution at pH 5.3. The PPy-MoP coating was formed by galvanostatic polymerization at 2.0 mA cm^{-2} for 500 s followed by polymerization at 1.0 mA cm^{-2} for 1,000 s in 0.2 M phosphoric acid solution containing 0.1 M pyrrole monomer and 5 mM $\text{PMo}_{12}\text{O}_{40}^{3-}$

two-step polymerization during immersion in 3.5 wt% NaCl aqueous solution at pH 5.3 for 4 days. In Fig. 4, the corrosion potential of bare steel was also plotted for comparison. The steel covered by the PPy-MoP coating reveals high potential in the passive region for 48 h and then decreases to about -0.4 V vs Ag/AgCl/Sat. KCl. In contrast, the potential of the bare steel is about -0.64 V . The potential suggests that the PPy-MoP coating stabilizes the passive film on the steel and makes the steel maintain the passive state for a long time period. Figure 5 shows the dissolution rate of Fe cations from the steel covered with the PPy-MoP coating during immersion in the same solution. In Fig. 5, corrosion potential was schematically plotted by the dotted line. The dissolution rate was evaluated from the amount of Fe ions dissolved in the solution sampled every 8 h. The average dissolution rate

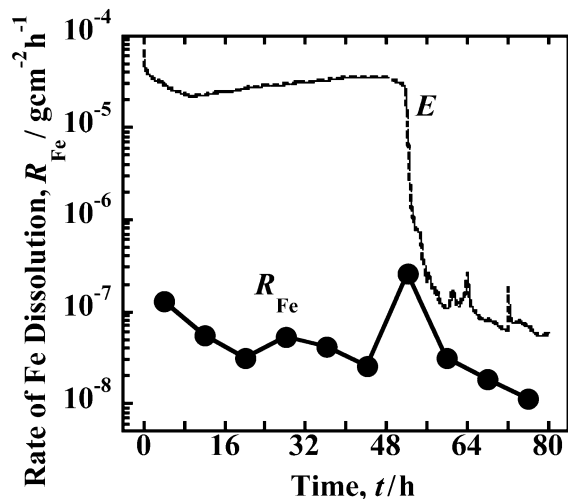


Fig. 5 Change in dissolution rate of Fe from the PPy-MoP-coated steel in neutral 3.5 wt% NaCl solution at pH 5.3. The PPy-MoP coating was the same as that in Fig. 4

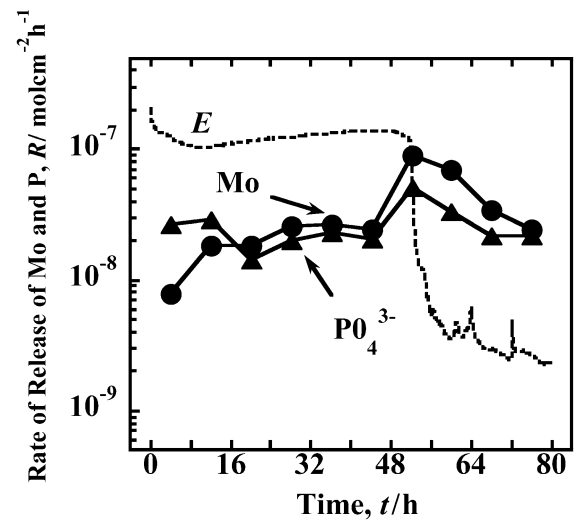


Fig. 6 Change in release rate of Mo ions and PO_4^{3-} from the PPy-MoP coating on the steels in neutral 3.5 wt% NaCl solution at pH 5.3. The PPy-MoP coating was the same as that in Fig. 4

during 80 h of immersion is about $7.1 \times 10^{-8} \text{ g cm}^{-2} \text{ h}^{-1}$, compared to $1.5 \times 10^{-5} \text{ g cm}^{-2} \text{ h}^{-1}$ for the bare steel. Hence, the dissolution rate of the steel covered with the PPy-MoP coating is inhibited by a factor of 200 as compared with the bare steel. The dissolution current evaluated from assumption of a reaction of $\text{Fe} = \text{Fe}^{3+} + 3e$ is $0.1 \mu\text{A cm}^{-2}$, which may be a typical value of passive current of iron in neutral solution. It is worth noting that the PPy-MoP coating inhibits the steel even after the potential drop to about -0.4 V which may not be in the passive region.

The doped anions of $\text{PMo}_{12}\text{O}_{40}^{3-}$ and PO_4^{3-} are released from the PPy coating during the immersion in the NaCl solution. Figure 6 shows release rates of Mo and phosphate ions into the aqueous solution. Phosphate ions are released at a relatively high rate of about $2.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ h}^{-1}$ in the

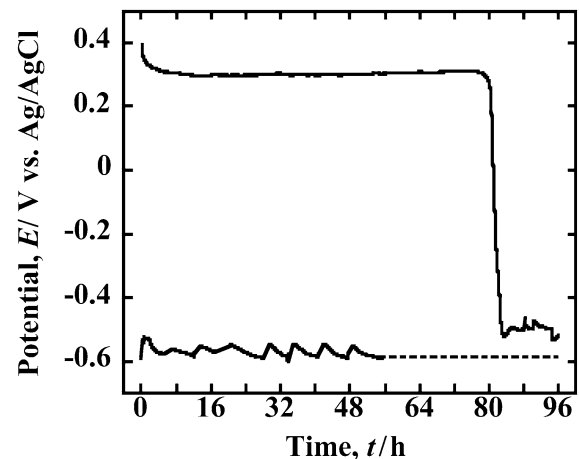


Fig. 7 Change in open circuit potential with time of the PPy-MoP coated steel and the bare steel in acidic 3.5 wt% NaCl solution at pH 1.9. The PPy-MoP coating was formed by galvanostatic polymerization at 2.0 mA cm^{-2} for 500 s followed by polymerization at 1.0 mA cm^{-2} for 1,000 s in 0.2 M phosphoric acid solution containing 0.1 M pyrrole monomer and 5 mM $\text{PMo}_{12}\text{O}_{40}^{3-}$

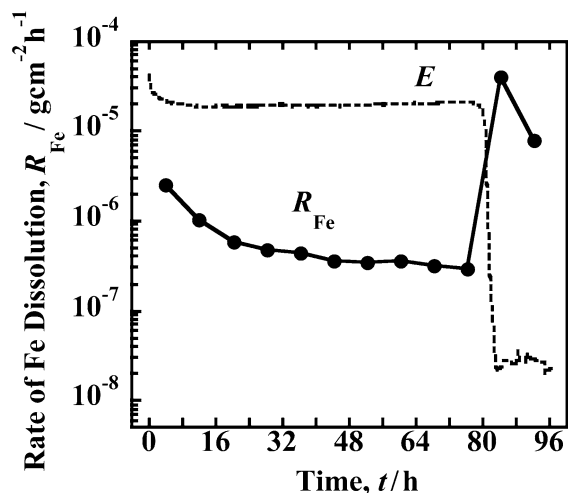


Fig. 8 Change in dissolution rate of Fe from the PPY–MoP-coated steel in neutral 3.5 wt% NaCl solution at pH 1.9. The PPY–MoP coating was the same as that in Fig. 7

initial 16 h and then at a rate of about $1\text{--}2 \times 10^{-8} \text{ mol cm}^{-2} \text{ h}^{-1}$ until 48 h. Mo ions whose form is assumed to be MoO_4^{2-} in this solution are released in the first-8-h stage at a relatively low rate less than $1 \times 10^{-8} \text{ mol cm}^{-2} \text{ h}^{-1}$, and then the release rate gradually increases to $2 \times 10^{-8} \text{ mol cm}^{-2} \text{ h}^{-1}$. The release of Mo ions and phosphate ions reveals a peak at 54 h of immersion, at which point the potential abruptly decreases from the passive potential region to -0.4 V .

The corrosion test was also done in acidic NaCl solution. Figures 7 and 8 show the corrosion potential and the dissolution rate of Fe, respectively, in the acidic 3.5 wt% NaCl solution at pH 1.9. The rate was evaluated from the amount of Fe^{3+} dissolving from the steel into the acidic

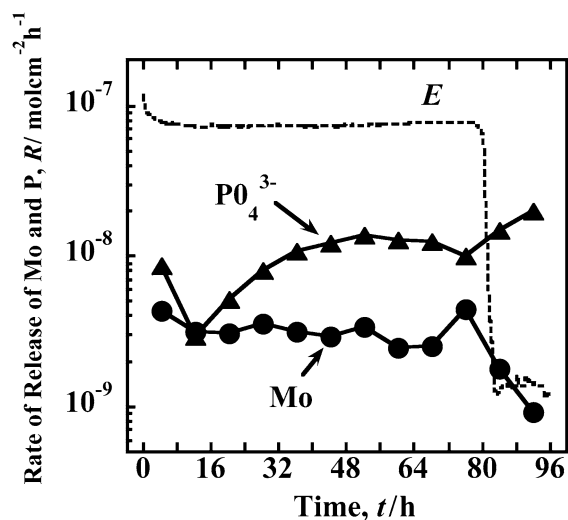


Fig. 9 Change in dissolution rate of Mo ions and PO_4^{3-} from the PPY–MoP coating on the steels in acidic 3.5 wt% NaCl solution at pH 1.9. The PPY–MoP coating was the same as that in Fig. 7

solution sampled every 8 h. The PPY-coated steel maintains a potential in the passive region until 80 h of immersion, then it decreases to about -0.5 V . The dissolution rate of the steel is about $6.8 \times 10^{-7} \text{ g cm}^{-2} \text{ h}^{-1}$ in average until 80 h. When one compared the value with the corrosion rate at $2.3 \times 10^{-4} \text{ g cm}^{-2} \text{ h}^{-1}$ measured for the bare steel in the acidic solution, the rate was found to be inhibited by a factor of 340 by the PPY–MoP coating. The dissolution current evaluated from assumption of the reaction of Fe to Fe^{3+} is about $1 \mu\text{A cm}^{-2}$, which may correspond to the passive current of steel in the acidic solution at pH 2. As shown in Fig. 9, the release rates of the dopants of molybdate and phosphate anions are about 3×10^{-9} and $1 \times 10^{-8} \text{ mol cm}^{-2} \text{ h}^{-1}$, respectively, both of which are smaller than those in the neutral NaCl solution.

Discussion

Preparation of the PPY–MoP coating

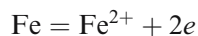
The PPY was easily formed by electrochemical anodic oxidation from the solution containing Py monomers and $\text{PMO}_{12}\text{O}_{40}^{3-}$ in phosphoric acid solution. The potential during the galvanostatic polymerization was much lower as compared with that reported in oxalate solution [16, 17, 19]. The hetero-polyanions may have a catalytic effect on the polymerization of Py to lower the polymerization potential. A low polymerization potential was also reported in the solution of *iso*-poly tungstate anions [26–28]. We also formed the PPY film in a neutral solution containing Py monomers and Na_2MoO_4 . The PPY film could be formed in the neutral solution, but many cracks were observed on the film surface after the film was dried in air. On the PPY film formed at the acidic aqueous solution in the present study, however, no such cracks were observed. The film formed in the acidic solution may be soft enough and stress-free to homogeneously cover the steel surface without cracks.

The PPY film electrochemically formed is doped by anions in the electrolyte solution. The PPY film formed in this study was found to be doped by anions of PO_4^{3-} and $\text{PMO}_{12}\text{O}_{40}^{3-}$. The measurements of the doped anions into the PPY coating by XPS and GD-OES will be described elsewhere. The doping of the anions was found from the corrosion test, in which the anions of Mo ions and PO_4^{3-} were released from the PPY film into the aqueous solution.

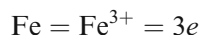
Corrosion prevention of steel by the PPY–MoP coating

It has been well known that the molybdate anions facilitate the formation of the passive oxide film and stabilize the passive films on steels. The hetero-polyanions $\text{PMO}_{12}\text{O}_{40}^{3-}$ doped in the PPY film are also expected to have a similar function at the interface between the substrate steel and the PPY film. The passive oxide film thus formed at the interface may decrease the dissolution current of steel.

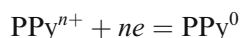
During the immersion in NaCl solution, an oxidation of Fe to Fe^{2+} or Fe^{3+} takes place through the passive oxide film.



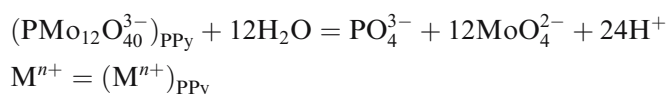
or



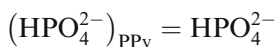
The oxidation is accompanied by reduction of PPy.



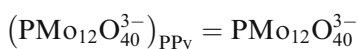
To maintain the neutrality in the coating, the reduction of PPy is further accompanied by release of doped anions to solution or uptake of cations from solution. In neutral solution, molybdo-phosphate poly-anions in the PPy–MoP coating gradually undergo hydrolysis to be decomposed to smaller anions and to be released more easily than the original poly-anions.



Phosphate anions doped as well are released simultaneously.



In acid solution, as the molybdo-phosphate poly-anions are more stable than in neutral solution, the release rate of dopants is supposed to become smaller as shown in Fig. 9.



When one assumes a series of the reactions from oxidation of the substrate steels to release of the doped anions via reduction of PPy without the influence of oxygen reduction, the dissolution current of Fe should be correlated with the release current evaluated from the release rate shown in Figs. 8 and 9. In the acidic NaCl solution, the release currents of molybdo-phosphate and phosphate anions are calculated to be 2×10^{-8} and 5.3×10^{-7} A cm^{-2} , respectively, and the total release current is about 5.5×10^{-7} A cm^{-2} . The release current may be comparable to the dissolution current of Fe at 1×10^{-6} A cm^{-2} , if the contribution of cation uptake is taken account. We believe that proton is incorporated into the PPy coating for charge compensation in acidic solution. [31] In the neutral NaCl solution, however, there is much difference between the dissolution current of Fe and the release currents of molybdo-

phosphate and phosphate anions; the release currents are 1.3×10^{-7} A cm^{-2} for molybdo-phosphate anions and 1.1×10^{-6} A cm^{-2} for phosphate anions, respectively. The total release current at about 1.2×10^{-6} is much larger than the dissolution current of Fe at 1×10^{-7} A cm^{-2} . When one assumes cation incorporation to the PPy coating instead of anion release from the coating, the discrepancy may become larger. A possible explanation for the discrepancy is the trapping of Fe ions or formation of Fe hydroxide in the PPy coating and not dissolving into the neutral solution. In this case, the oxidation rate of Fe or corrosion rate is expected to be larger than the dissolution rate of Fe measured. The other explanation is the replacement of the dopant anions with chloride ions in the solution. The exchange reaction can proceed without oxidation of Fe and reduction of the PPy.

The PPy–MoP coating is thus changed to a reduced state gradually with the oxidation of substrate steel and loses the capability to maintain the passive state of the steel. Finally, the substrate steel transfers from the passive state to the active state under the reduced PPy film.

In order that substrate steels maintain the passive state for a longer time period, a further improvement of the PPy coating will be required. When one considered a series of the above reactions, it is assumed that the corrosion rate of steel is lowered, if some steps in the above reactions can be inhibited. Degradation of PPy coatings is induced by simultaneous reactions of reduction of PPy matrix and of removal of doped anions or uptake of cations. If one can stop the dedoping process of anions from the matrix and the uptake process of cations, it is expected that the life of the PPy coating for corrosion prevention can be prolonged. Such improvement is in planning by introducing a bipolar-structured PPy.

Conclusion

The polypyrrole coating on carbon steel was prepared from phosphoric acid solution containing pyrrole monomer and molybdo-phosphate poly-anions $\text{PMo}_{12}\text{O}_{40}^{3-}$ to prevent corrosion of the substrate steel:

- (1) The polypyrrole anodically prepared was doped by $\text{PMo}_{12}\text{O}_{40}^{3-}$ and PO_4^{3-} and was flexible enough to cover the steel homogeneously without cracks.
- (2) The 5.1-mm-thick polypyrrole coating makes the steel maintain the passive state for 48 h in neutral 3.5 wt% NaCl solution at pH 5.3 and for 80 h in acidic 3.5 wt% NaCl solution at pH 1.9. The dissolution current of the steel during the immersion remains at the level of the typical passive current in the respective solutions.

Acknowledgement The present work was partially supported by ISIJ Research Promotion Grant of the Iron and Steel Institute of Japan.

References

1. DeBerry DW(1985) *J Electrochem Soc* 132:1022
2. Malik MA, Galkowski MT, Bala H, Grzybowska B, Kulesza PJ (1999) *Electrochim Acta* 44:2157
3. Gasparac R, Martin C-R (2001) *J Electrochem Soc* 148:B138
4. Gasparac R, Martin C-R (2002) *J Electrochem Soc* 149:B409
5. Su W, Iroh JO (1997) *Electrochim Acta* 42:2685
6. Kraljic M, Mandic Z, Duic Lj (2003) 45:181
7. Cheung KM, Bloor D, Stevens GC (1988) *Polymer* 29:1709
8. Schirmeisen M, Beck F (1989) *J Appl Electrochem* 19:401
9. Fenelson AM, Breslin CB (2002) *Electrochim Acta* 47:4467
10. Bazzaoui M, Martin L, Bazzoui EA, Martin JI (2002) *J Electroanal Chem* 537:47
11. Tallman DE, Vang C, Wallace GG, Bierwagen GP (2002) *J Electrochem Soc* 149:C173
12. Deng Z, Smyrl WH, White H (1989) *J Electrochem Soc* 136:2152
13. Fenelon AM, Breslin CB (2003) *Corros Sci* 45:2837
14. Wessling B (1994) *Adv Mater* 6:1994
15. Lu W-K, Elsenbaumer RL, Wessling B (1995) *Synth Met* 71:2163
16. Beck F, Michaelis R, Schloten F, Zinger B (1994) *Electrochim Acta* 39:229
17. Krstajic NV, Grgur BN, Sovanovic SM, Vojnovic MV (1997) *Electrochim Acta* 42:1685
18. Su W, Iroh JO (1999) *Electrochim Acta* 44:2173
19. Su W, Iroh JO (1999) *Electrochim Acta* 44:3321
20. Su W, Iroh JO (2000) *Electrochim Acta* 46:1
21. Nguyen H, Li T, Garcia B, Deslouis C, Xuan L (2001) *Electrochim Acta* 46:4258
22. Hammache H, Makhloufi L, Saidani B (2003) *Corros Sci* 45:2031
23. Nguyen Thi Le H, Garcia B, Deslouis C, Le Xuan Q (2001) *Electrochim Acta* 46:26
24. Nguyen Thi Le H, Garcia B, Deslouis C, Le Xuan Q (2002) *J Electroanal Chem* 32:105
25. Hien NTL, Garcia B, Paillet A, Deslouis C (2005) *Electrochim Acta* 50:1747
26. Hammache H, Makhloufi L, Saidani B (2003) *Corros Sci* 45:2031
27. Garcia B, Lamzoudi A, Piller E, Nguyen Thi Le H, Deslouis C (2002) *J Electrochem Soc* 149:B560
28. Lapkowski M, Biden G, Fournier M (1991) *Synth Met* 41:407
29. Dong S, Jin W (1993) *J Electroanal Chem* 354:87
30. Cheng SA, Otero TF (2002) *Synth Met* 129:53
31. Ohtsuka T, Wakabayashi T, Einaga H (1994) *J Electroanal Chem* 377:107
32. Takahashi M, Tsuchida T, Ohtsuka T (1996) *Thin Solid Films* 280:124
33. Ohtsuka T, Wakabayashi T, Einaga H (1996) *Synth Met* 79:235