

Poly(2,5-dimethoxyaniline) film coating for corrosion protection of iron

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Abstract A poly(2,5-dimethoxyaniline) (PDMA) film was coated on the iron surface by the electropolymerization of 2,5-dimethoxyaniline in neutral buffer solution (pH 6.86). The PDMA film strongly adhered to the surface because of the polar methoxy groups of the PDMA molecules. The fact that no electrochemical response of the PDMA film-coated iron electrode to dissolved Fe^{2+} exhibited that the PDMA film was less permeable to dissolved species, acting as a diffusion barrier against agents causing corrosion such as H_2O and O_2 . The PDMA film coating greatly lowered the anodic current peak ascribed to the anodic dissolution of iron and the corrosion current in strongly acidic medium, 0.5 M H_2SO_4 aqueous solution (1 M=1 mol dm $^{-3}$) as well as neutral medium (pH 6.86). The high anti-corrosion ability was due to a hybrid effect of the PDMA film not only as the diffusion barrier, but also as an in situ oxidant in spite of the slight redox activity of PDMA. In addition, the PDMA film is much more durable and adhesive than polyaniline film against over-oxidation.

Keywords Poly(2,5-dimethoxyaniline) · Iron · Corrosion protection · Corrosion current · Conductive polymer

Introduction

It goes without saying that the corrosion of metals is unfavorable phenomena for practical use. So far, to protect the corrosion, there are mainly four methods: (1) simply coating the metal with a material, such as epoxy, enamel, and alkyd resin, which physically impedes the causing corrosion; (2) the use of chemical conversion coatings such as chromates to alter the metal surface for protection; (3) cathodic protection, where a small negative potential continuously applied to the metal surface to make it passive; (4) anodic protection, where charge (e^-) is withdrawn from a metal to keep the metal in oxidized state rendering it passive to corrosion. Unfortunately, however, the coatings in the methods (1) and (2) are powerless against the formation of cracks and/or pinholes. On the other hand, the methods (3) and (4) are more cumbersome and expensive than most methods.

The coatings of conductive polymer films are more effective, cheaper, and also more environmentally friendly than the methods described previously [1]. Even though pinholes and/or cracks are formed in the coatings, the anti-corrosion ability is barely lowered because of the principles of the anti-corrosion coatings. The oxidized form of p-type conductive polymers has been employed as the coatings. The coating is said to simply serve as an in situ oxidant or anodic protectant [2, 3]. At the same time that the coating oxidizes the metal surface where it is contact with, it is getting reduced itself. Since the reduced coating is re-oxidized by ambient air, it continues to oxidize the metal surface, and the passive state is maintained.

Among conductive polymers, it is widely recognized that polyaniline (PANI) film has been one of the best candidate conductive polymer films for an anti-corrosion coating since the anti-corrosion ability was found [4, 5].

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Although many studies about the anti-corrosion ability of PANI have been performed [5–28], effort to enhance the ability should be necessary before practical use. Besides, the adhesion of electrodeposited PANI film coating is generally quite poor against iron and steel [29], and this adhesion problem should be solved. If the PANI molecules had polar functional groups, their adhesion ability would be enhanced. Several PANIs having polar functional groups have successfully been prepared as films on the electrode surface. It is expected that high adhesion ability is obtained more frequently in ring-substituted PANI films than in N-substituted ones and in di-substituted ones than mono-substituted ones. For this reason, in this study, poly(2,5-dimethoxyaniline) (PDMA) film is employed to solve the adhesion problem as well as to enhance the anti-corrosion ability. Although the fact that the PDMA film has the anti-corrosion ability has already been reported [30, 31], the stability as well as the anti-corrosion ability of the PDMA film is examined mainly using electrochemical measurements. The film is strongly adhesive to the iron surface and shows a good anti-corrosion ability because it behaves not only as the diffusion barrier, but also as the in situ oxidant. In addition, the PDMA film is much more durable and adhesive than polyaniline film against over-oxidation.

Experimental details

Electrochemical measurements

An electropolymerization and three kinds of electrochemical measurements, cyclic voltammogram, linear sweep voltammogram, and steady-state polarization curve, were carried out with a Hokuto Denko HZ-3000 electrochemical measurements system, using a standard three-electrode cell. A Hokuto Denko HX-C7 Pt plate electrode and a Hokuto Denko HX-R3 Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All the electrochemical measurements were performed at room temperature.

Materials and preparation

The monomer, 2,5-dimethoxy aniline (Wako Pure Chemical Industry Co.), was reagent grade and were distilled under reduced pressure prior to use. Other chemicals employed in this study were of reagent grade and were used without further purification.

Aqueous solutions were prepared using distilled deionized water. The iron electrode used as the working electrode was an iron disk electrode. An iron rod cut from a commercial iron nail (#2-080-00125) was embedded in a Teflon rod. The area of the disk electrode was 0.16 cm². In addition, a Hokuto Denko HR-D2 Pt disk electrode was

used for the electrochemical measurements of the redox activity of the PDMA film and of the electrochemical response to dissolved Fe²⁺.

Results and discussion

Preparation of the PDMA film coating

The PDMA film was coated on the electrode surface by electro-oxidizing the monomer: 5 mM 2,5-dimethoxyaniline in an Aldrich phosphate buffer aqueous solution whose pH was 6.86 to prevent the iron surface from corroding. Potential sweep electrolytic mode was employed to electro-oxidize the monomer. The switching potential in the positive scan was +1.0 V, where the oxygen evolution did not occur. It is widely accepted that the potential scan number (*N*) during the electropolymerization corresponds to the deposited amount on the electrode surface. In other words, the thickness of the deposited PDMA film can be determined by *N*. The PDMA film-coated electrodes were rinsed with adequate water to remove the monomers and oligomer species, which will affect the voltammograms.

Figure 1 shows typical cyclic voltammograms during the electropolymerization of 5 mM 2,5-dimethoxyaniline in an Aldrich phosphate buffer aqueous solution (pH 6.86). In the first positive scan, irreversible anodic current is observed from about 0.5 V. The current is probably due to the oxidation of 2,5-dimethoxyaniline to the dication. The anodic current rapidly decreases with an increase of *N*. This means that the deposited PDMA film has only a little conductivity. This stops the anodic current from flowing. The redox current peak at around 0.25 V is ascribed to the redox reaction of the deposited PDMA film on the electrode

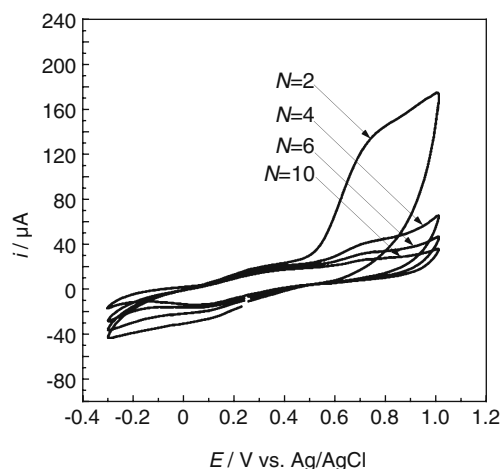


Fig. 1 Cyclic voltammograms at 50 mV/s during the electropolymerization of the monomer, 2,5-dimethoxyaniline (0.5 mM), in pH 6.86 buffer solution at *N*=2, 4, 6, and 10

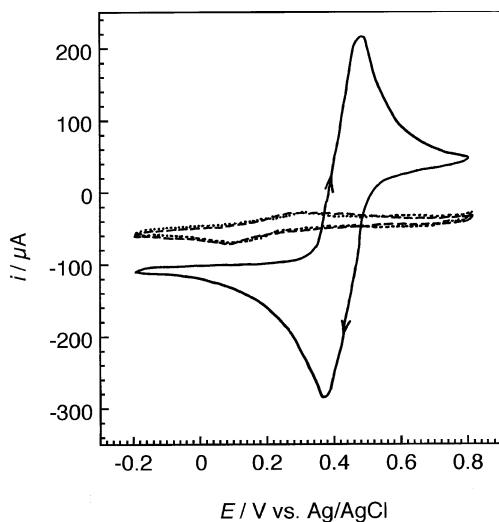


Fig. 2 Cyclic voltammograms showing the electrochemical response of the iron (*line*) and the PDMA film-coated Fe electrode (*broken line*) to 10 mM $\text{Fe}(\text{CN})_6^{3-}$ in a pH 6.86 buffer solution at 50 mV/s. The cyclic voltammogram showing the redox activity of the electro-deposited PDMA film in a pH 6.86 buffer solution is also shown (*dotted line*)

surface although the peak height is slight. The redox peak potential is low enough to enable the reduced form of PDMA (PDMAred) to be changed to the oxidized form (PDMAox) by the ambient air. In addition, the electropolymerization was stopped at $N=10$ unless otherwise noted.

The PDMA film was coated on the iron electrode, and the electrochemical response to dissolved Fe^{2+} was examined to confirm whether the film blocked dissolved species. The cyclic voltammogram is shown in Fig. 2. The reversible redox current peak of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is evident, while the peak vanishes by the PDMA film coating. This fact exhibits that the electrodeposited PDMA film is less permeable to dissolved species.

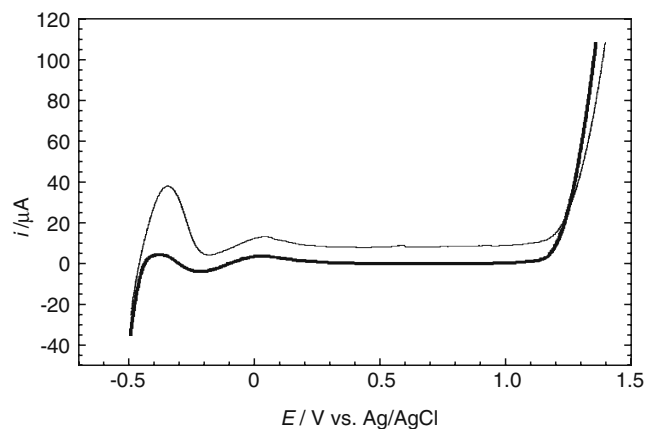


Fig. 3 Linear sweep voltammograms at 5 mV/s measured with a bare iron (*thin line*) and the PDMA film-coated iron (*thick line*) electrodes in a pH 6.86 buffer solution

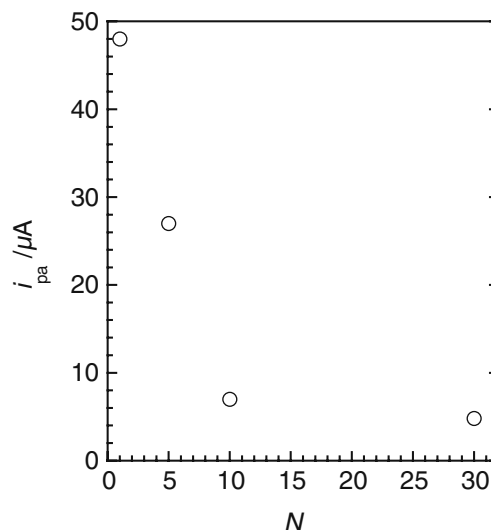


Fig. 4 Relationship between the deposited amount of the PDMA film (N) and i_{pa}

Suppression of anodic current of iron

To investigate the anti-corrosion ability of the PDMA film coating, linear sweep voltammograms were firstly measured using the PDMA film-coated iron electrodes in air-saturated neutral aqueous solution (pH 6.86). The linear sweep voltammograms are shown in Fig. 3. The anodic current peak at around -0.49 V is scribed to the anodic dissolution of iron. As expected, the PDMA film coating effectively suppresses the current peak; in other words, the PDMA film coating prevents the anodic reaction of the iron corrosion from occurring.

It is practically important to determine what deposited amount of the PDMA film shows the best anti-corrosion ability. The amount varied with N during the electro-

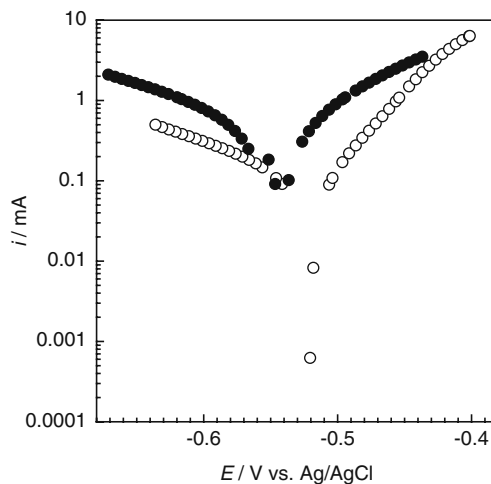


Fig. 5 Tafel plots obtained from the polarization curves measured using a bare iron (*circle*) and the PDMA film-coated iron (*filled circle*) electrodes in 0.5 M H_2SO_4 aqueous solution

Table 1 Corrosion current (i_{corr}) and potential (E_{corr}) determined by the extrapolation of the Tafel region of the cathodic and anodic polarization curves

Coating	Acidic solution (0.5M H ₂ SO ₄)		Neutral buffer solution (pH6.86)	
	E_{corr} (V)	i_{corr} (mA)	E_{corr} (V)	i_{corr} (mA)
None	-0.519	0.676	-0.699	0.0306
PDMA film	-0.533	0.184	-0.635	0.0042

polymerization. The PDMA film coatings with different N values were prepared on the Fe electrode; the linear sweep voltammograms were measured in an air-saturated neutral aqueous solution (pH 6.86). The relationship between N and the anodic peak current (i_{pa}) is shown in Fig. 4. The i_{pa} value significantly decreases with N and roughly becomes constant when N exceeds 10. This suggests that the PDMA film with $N \geq 10$ has a sufficient anti-corrosion ability.

Corrosion current and potential

In order to determine the kinetic parameters, the corrosion current (i_{corr}), and potential (E_{corr}), the steady-state polarization curves were measured for the PDMA film coating in acidic and neutral aqueous solutions. The typical Tafel plots obtained from the polarization curves are shown in Fig. 5. The oxidation and reduction branches of the curves are well defined. The extrapolation of the Tafel regions of the cathodic and anodic polarization curves is used to obtain i_{corr} and E_{corr} . It yields a lower i_{corr} , reflecting the anti-corrosion ability (Table 1).

Anti-corrosion mechanism

The PDMA film strongly adheres to the Fe surface and plays two important roles, i.e., a diffusion barrier and in situ oxidant. The film is less permeable to dissolved species, thus acting as a diffusion barrier that physically impedes the agents causing corrosion, such as H₂O, O₂, and salt. On the other hand, because of the redox activity, the film also acts as an in situ oxidant. The PDMA film must contribute to electrocatalytic reduction of oxygen in analogy with polyaniline film [34, 35].

Stability of the PDMA film against over-oxidation

It is widely accepted that an electrodeposited polyaniline film loses redox activity and is liable to be detached from the electrode substrate [32, 33]. In order to examine the stability to over-oxidation, the PDMA film-coated electrode was polarized at 1.2 V, where the over-oxidation of polyaniline occurs frequently. The relationship between the redox charge of the PDMA film (Q) and the polarization time (t) is shown in Fig. 6. In addition, Q was determined by the graphical integration of the

corresponding cyclic voltammogram. The relationship for the polyaniline film is also shown for comparison. The polyaniline film has little redox charge at $t=30$ min. The redox current of Fe²⁺/Fe³⁺ shown in Fig. 2 was observed using the polyaniline film-coated electrode. The film was easily detached from the electrode substrate. Compared the polyaniline film, the PDMA film still has about 65% redox charge at $t=30$ min compared to the original redox charge (Q_0) and the film adhered to the electrode substrate. The redox current of Fe²⁺/Fe³⁺ was not observed using the PDMA film-coated electrode experienced the polarization for 30 min.

Conclusions

To protect Fe from corrosion, the PDMA film was electrochemically coated on the Fe surface, which strongly adhered to the surface because of the polar methoxy groups. The PDMA film was less permeable to dissolved species, thus acting as the diffusion barrier. The barrier physically impeded the agents causing corrosion, such as H₂O and O₂. On the other hand, the film acted as an in situ oxidant holding the Fe surface in the passive state. As a result, the PDMA film coating protected the corrosion electrochemi-

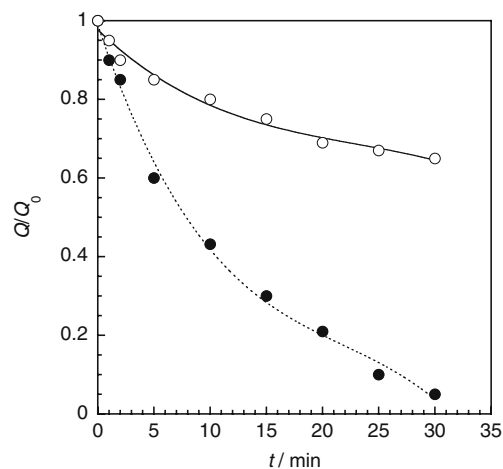


Fig. 6 Relationship between the redox charge (Q) and the polarization time (t) at 1.2 V in 0.5 M H₂SO₄ aqueous solution. Q_0 original redox charge before the polarization. Circle PDMA film, filled circle polyaniline film

cally as well as physically. In addition, the PDMA film is much more durable and adhesive than polyaniline film against over-oxidation.

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