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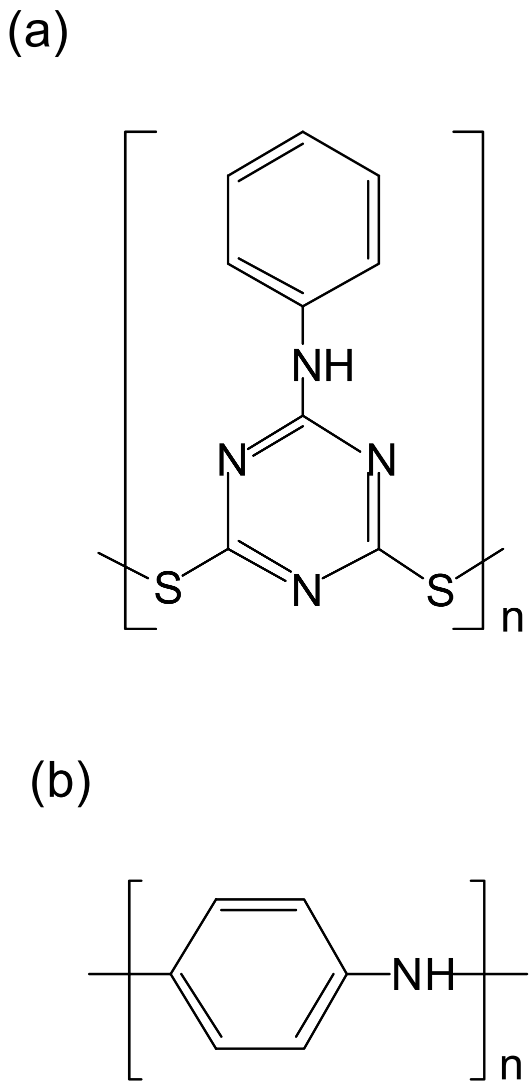
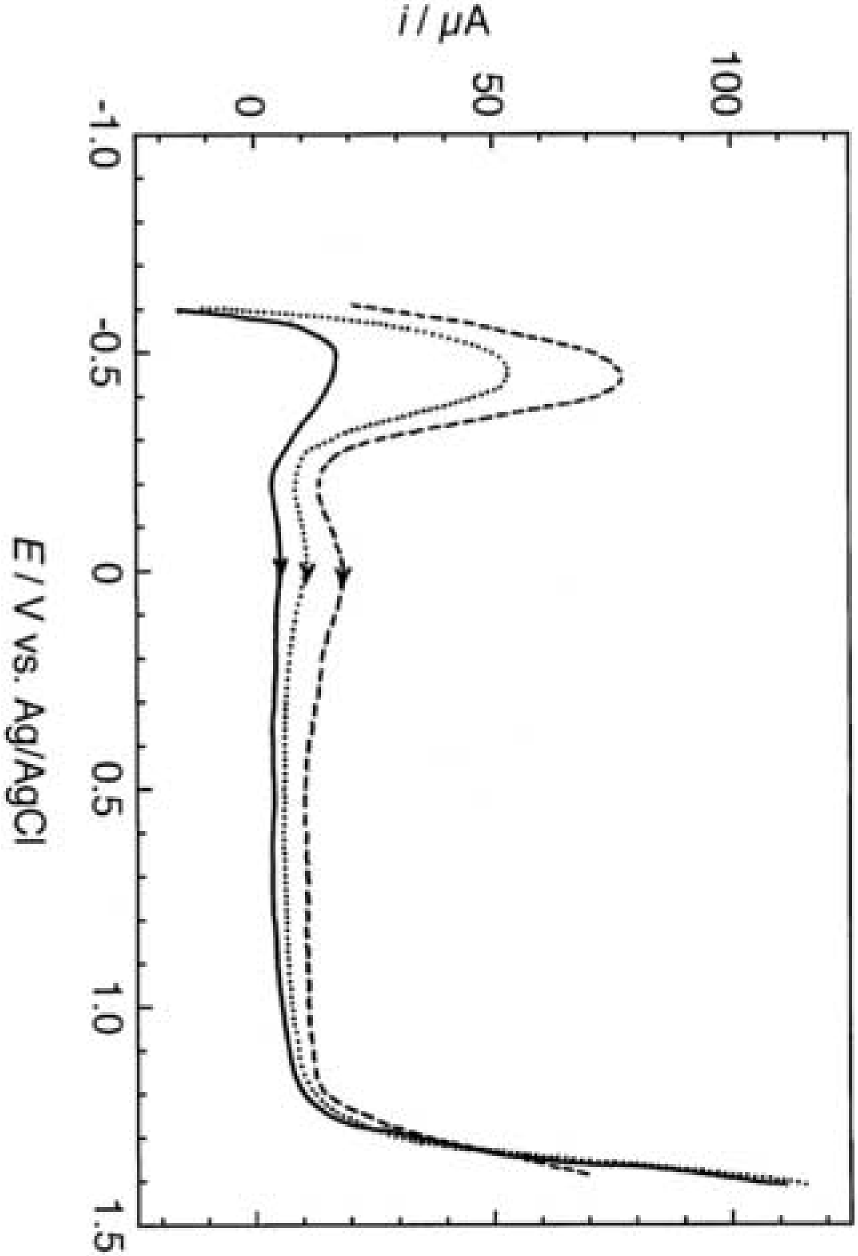


Figure 1 Jun Yano et al.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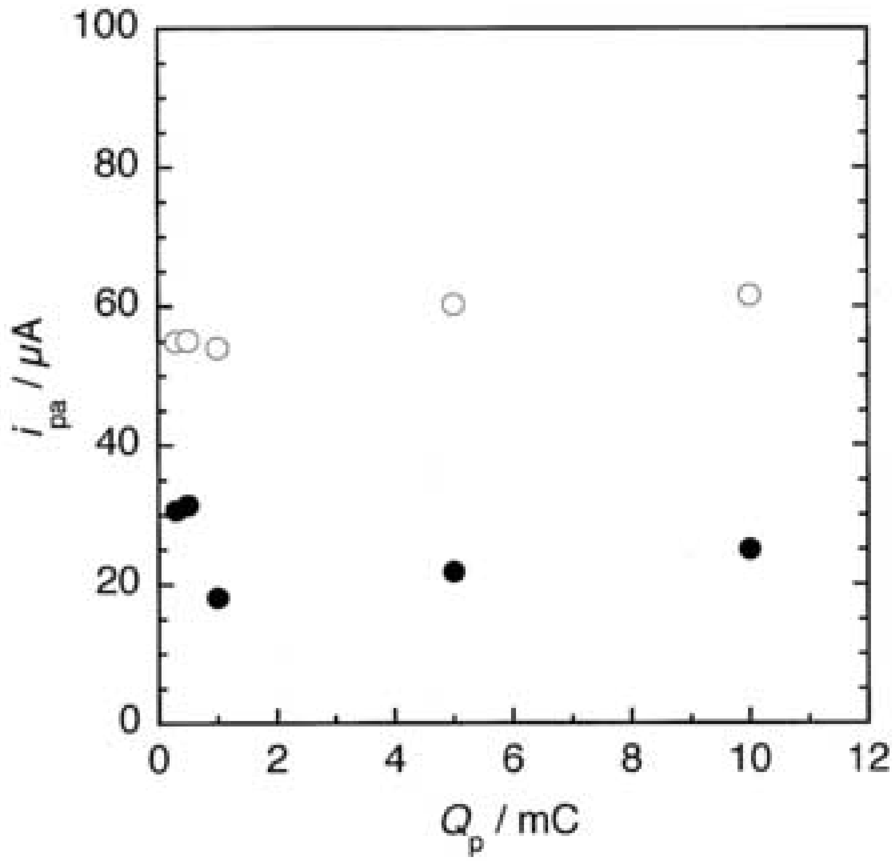
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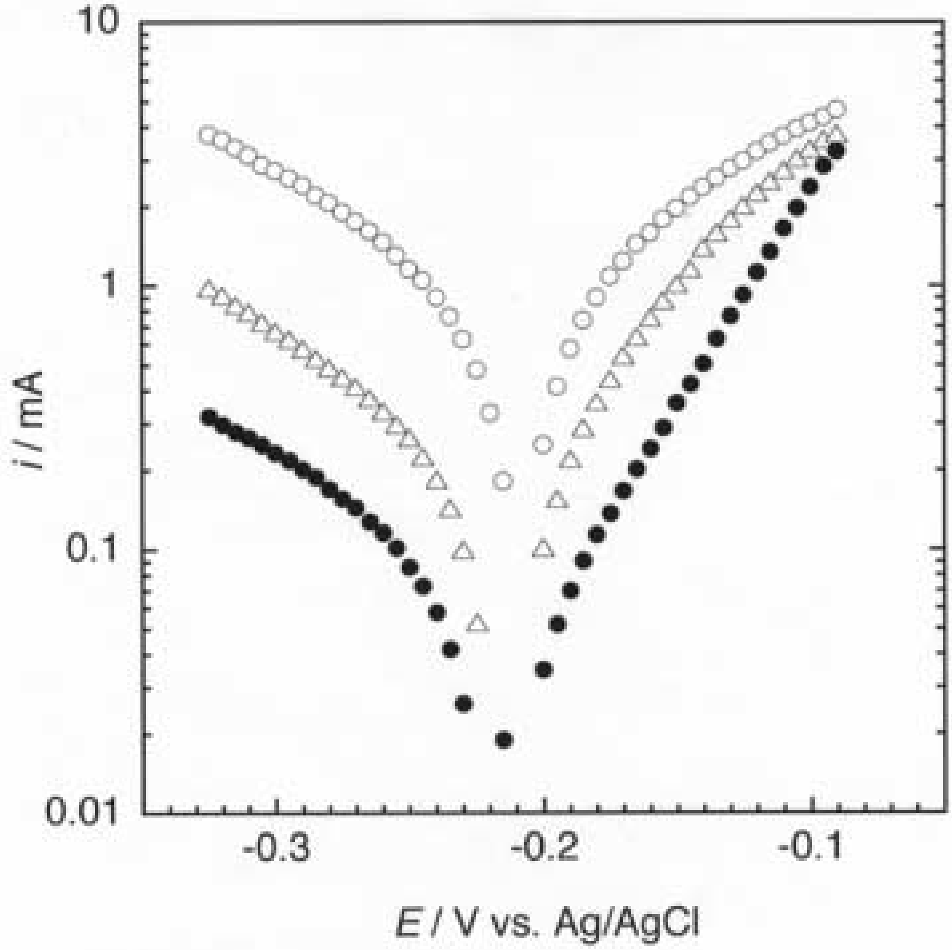
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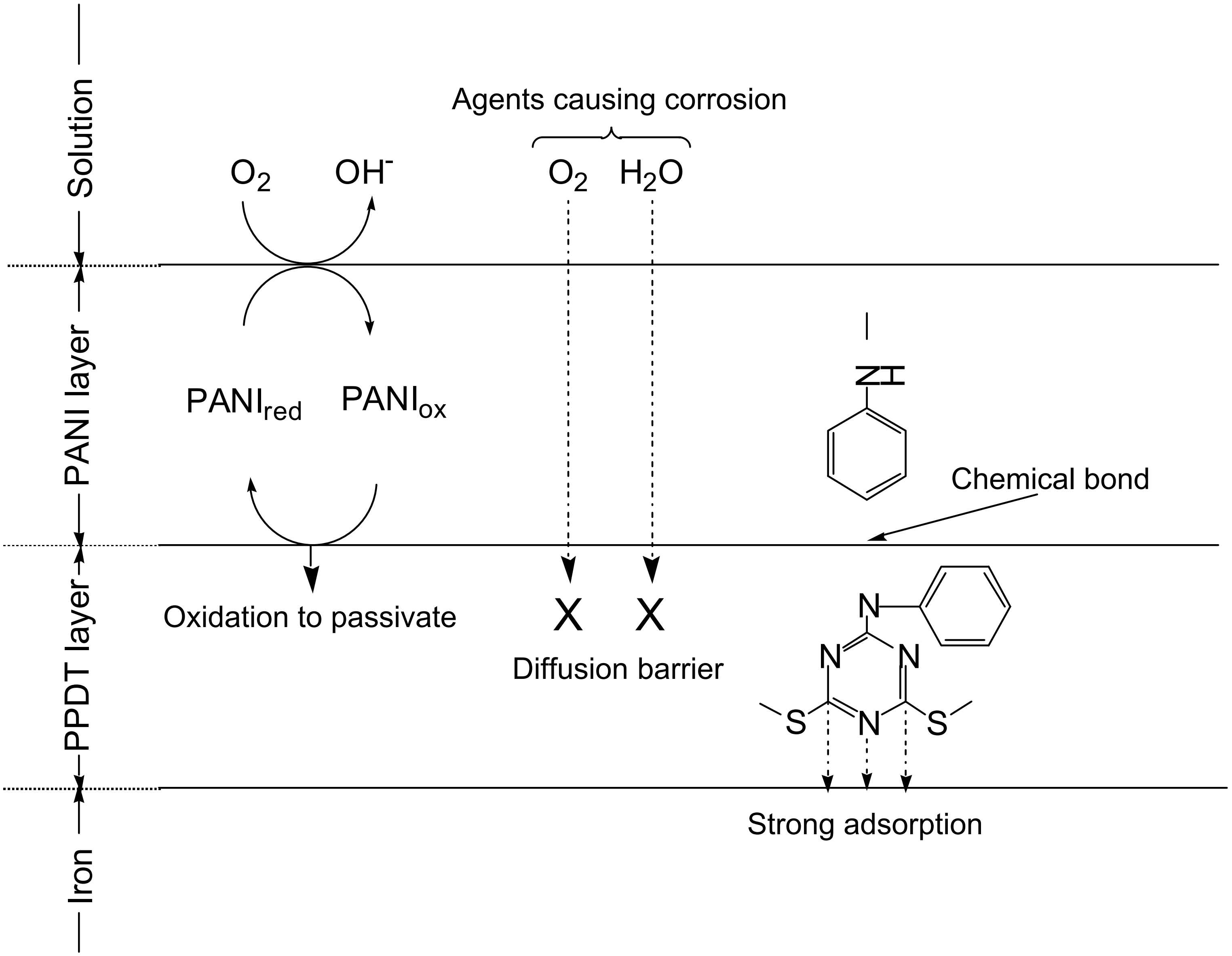

Figure 5 Jun Yano et al.

Table 1

Corrosion current (i_{corr}) and potential (E_{corr}) determined by the extrapolation of the Tafel regions of the cathodic and anodic polarization curves in Fig. 4.

Coating	E_{corr} / V *vs*. Ag/AgCl	i_{corr} / mA
None	-0.212	0.75
PPDT layer	-0.229	0.23
PANI/PPDT double-layer	-0.209	0.06

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Bilayer polymer coating containing a polyaniline for corrosion protection of iron

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Abstract

A poly(2-*N*-phenylamino-4,6-dimercapto-S-triazine) (PPDT) layer was first prepared electrochemically on an iron surface. The PPDT layer strongly adsorbed on the surface because of the polar triazine rings of the PPDT molecules. No electrochemical response of the PPDT layer covered electrode to dissolved $Fe(CN)_6^{3-}$ was observed. This fact indicated that the PPDT layer is an insulating layer with low permeability to dissolved species, and thus acting as a diffusion barrier against agents causing corrosion such as H_2O and O_2. A polymer polyaniline (PANI) layer was electrodeposited on the PPDT layer. This system was conductive because electron transfer through the PPDT layer occurred by electrons hopping utilizing the localized electron density of the triazine ring. The obtained PANI/PPDT bilayer coating greatly lowered the anodic current peak ascribed to the anodic dissolution of iron and the corrosion current. The high anti-corrosion ability was due to a hybrid effect of the PANI layer as an *in-situ* oxidant and the PPDT layer as a diffusion barrier.

Key words: Anti-corrosion, Iron, Polyaniline, poly(2-*N*-phenylamino-4,6-dimercapto-S-triazine), Double-layer coating.

1. Introduction

Among various materials for anti-corrosion of metals, conductive polymer coatings are one of the most effective, cheapest and also most environmentally friendly materials [1]. Even though pinholes and/or cracks are formed in the coatings, the anti-corrosion ability is barely lowered because of the features of the anti-corrosion coatings. The coatings are said to serve simply as an *in-situ* oxidant or anodic protectant [2,3]. At the same time that the coating oxidizes the metal surface to which it is in contact, it is reduced. 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) has been one of the best candidate of conductive polymers for an anti-corrosion coating since the anti-corrosion ability was found [4,5]. Although numerous studies about the anti-corrosion ability of PANI have been performed [5-28], effort to enhance the ability is necessary for practical use [5-28]. For example, the adhesion problem must be solved. The adhesion of an electrodeposited PANI coating is generally quite poor against iron and steel [29]. In order to solve the adhesion problem as well as to enhance the anti-corrosion ability, our strategy is to employ a double-layer coating comprised of PANI and poly(2-*N*-phenylamino-4,6-dimercapto-S-triazine) (PPDT), which we first prepared (Fig. 1).

Fig. 1

2. Experimental

One of the monomers, aniline (Wako Pure Chemicals Co.), was distilled under reduced pressure prior to use. The other monomer, 2-*N*-phenylamino-4,6-dimercapto-S-triazine (Sankyo Kasei Co.), was of reagent grade and as used without further purification. Other chemicals employed in this study were of reagent grade and were used without further purification. Aqueous solutions were prepared using distilled deionized water An 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 insulator. The area of the disk electrode was 0.16 cm^2. A Hokuto Denko HR-D2 Pt disk electrode was used for the electrochemical response of PPDT, PANI and PANI/PPDT double-layer coated electrodes. Electrochemical measurements 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. The electrodeposition of PANI and PPDT was made by electro-oxidizing the monomer: 0.1 M (1 M = 1 mol dm^{-3}) aniline in an Aldrich phosphate buffer aqueous solution (pH 6.86) and 5 mM 2-*N*-phenylamino-4,6-dimercapto-S-triazine in 0.1 M Na_2CO_3 aqueous solution. Either potential sweep (-0.3 ~ +1.0 V at 50 mV s^{-1}) or 1.0 V constant-potential electrolytic mode was employed to electro-oxidize the monomer. Both PANI and PPD could be was electrodeposited with either mode.

3. Results and Discussion

To examine how the PPDT and PANI/PPDT bilayer coatings suppress corrosion, linear sweep voltammograms were measured with the PPDT and the PANI/PPDT bilayer coated electrodes in air-saturated neutral aqueous solution (pH 6.86). Both the PPDT and PANI/PPDT bilayer coatings were prepared by the constant-potential electro-oxidation of the corresponding monomer at 1.0 V. The electro-oxidation was carried out until the passed charge was 1 mC. The linear sweep voltammograms are shown in Fig. 2. The anodic current peak at around -0.45 V is ascribed to the anodic dissolution of iron. As expected, the PANI/PPDT bilayer coating suppresses the current peak most effectively.

Fig. 2

It is important to know what thickness of the PPDT layer shows the best anti-corrosion ability. The thickness varied with the charge passed during the electrodeposition (Q_p). The PPDT and PANI/PPDT bilayer coatings with different Q_p were prepared on the iron electrode; the linear sweep voltammograms were measured in air-saturated neutral aqueous solution (pH 6.86). The relationship between Q_p and the anodic peak current (i_{pa}) is shown in Fig. 3. The i_{pa} value is roughly constant regardless of Q_p although it fluctuates slightly. This suggests that a thin PPDT layer is adequate to acquire the anti-corrosion ability. In addition, the thickness of the PANI layer corresponding to a Q_p of 0.3 mC was adequate to show the same anti-corrosion ability.

Fig. 3

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 PPDT and PANI/PPDT bilayer coatings in acidic and neutral aqueous solutions. The typical Tafel plots obtained from the polarization curves are shown in Fig. 4. 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 smaller i_{corr}, reflecting the anti-corrosion ability (Table 1). In addition, E_{corr} is almost the same in any case.

Fig. 4

The PPDT layer plays three important roles: (1) diffusion barrier, (2) adhesive binder and (3) electron transfer medium between the iron substrate and the PANI layer. The PPDT layer is an insulating layer with less permeability to dissolved species [30,31], acting as the diffusion barrier. The barrier physically impedes the agents causing corrosion such as H_2O, O_2 and salt. The PPDT layer adsorbs to the iron substrate more strongly than PANI because of the polar triazine rings of the PPDT molecules. The amino groups of the PPDT molecules enable the chemical combining of the PPDT molecules with the PANI molecules. The electron transfer through the PPDT layer occurs by electron hopping utilizing the localized electron density of the triazine ring [30,31]. This proposed mechanism is schematically depicted in Fig. 5. The key material, PPDT, is expected to allow preparation of other bilayer coatings containing different conductive polymers and to be applied to various metal corrosion problems because of the anticipated novel and unique properties.

Fig. 5

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Figure captions

Fig. 1. Probable molecular backbones of polyaniline (PANI) and poly(2-*N*-phenylamino-4,6-dimercapto-S-triazine) (PPDT).

Fig. 2 Linear sweep voltammograms at 5 mV s^{-1} measured with a bare iron (------), PPDT layer (…………………) and PANI/PPDT double-layer (– – – –) coated electrodes in a neutral Aldrich phosphate buffer solution (pH 6.86.

Fig. 3 Relationship between the charge passed during the electrodeposition of the PPDT layer (Q_p) and the anodic peak current ascribed to the anodic dissolution of iron (i_{pa}).

(○): PPDT layer coated iron electrode.

(•): PANI/PPDT double-layer coated electrode.

Fig. 4 Tafel plots obtained from the polarization curves measured with a bare iron (○), PPDT layer (▵) and PANI/PPDT double-layer (•) coated electrodes in 0.5 M H_2SO_4 aqueous solution.

Fig. 5 Schematic depiction explaining the anti-corrosion mechanism of the PANI/PPDT double-layer coating on an iron surface.