

Synthesis of oxalate doped polyaniline and its corrosion protection performance

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Abstract It is known that dopants present in polyaniline (PANI) play an important role in corrosion protection of mild steel since the dopant ions form a secondary layer with iron. Since oxalate ions form a stable iron oxalate layer on mild steel, a study has been made on the corrosion protection performance of steel by vinyl coating containing oxalate doped PANI in acid and neutral media. Electrochemical impedance spectroscopy (EIS) studies have shown that the oxalate doped PANI is able to protect mild steel in sodium chloride solution since the impedance values are maintained at $10^{10} \Omega \text{ cm}^2$ even after 100 days of exposure.

Keywords Organic coatings · Mild steel · EIS · IR spectroscopy · XRD · Passivity · Paint coatings

Introduction

Conducting polymers are promising candidate materials as a replacement for the hexavalent chromates in corrosion protection [1, 2]. Polyaniline (PANI) containing organic coatings have been found to protect iron from corrosion in acid and neutral media [3–5]. The mechanism of corrosion protection of iron by PANI containing coating has been reported to be the formation of passive oxide layer due to redox reaction between PANI and iron surface [6–11]. Besides the redox property of PANI, it is reported that the dopant ions form a secondary layer with iron surface, which also give additional protection [12–15]. Since oxalate ions

form iron oxalate layer by reaction with iron, a study has been made on the corrosion protection performance of oxalate doped PANI containing organic coating on iron, and the results are reported in the paper.

Experimental

Preparation of oxalate doped PANI pigment

PANI was obtained by oxidative polymerization of distilled aniline in HCl using ammonium persulphate as oxidant [15]. One molar distilled aniline was dissolved in 500 ml of 1 M solution of HCl. Pre-cooled 1 M solution of ammonium persulphate was added drop-wise to the pre-cooled aniline–acid mixture for about 1.5 h with constant stirring. The reaction was conducted at $5 \pm 1 \text{ }^\circ\text{C}$. After the addition, the stirring was continued for 3 h for ensuring complete polymerization. A dark green colored conducting PANI thus formed was filtered and repeatedly washed with distilled water to remove excess acid content. The polymer was dried in oven at about $80 \text{ }^\circ\text{C}$ for 2 h. The dried PANI was fine-grinded using a mortar. The synthesized PANI was dedoped by dispersing and stirring in 1 M NH_4OH for 5 h. The dedoped PANI was filtered and dried. Redoping of PANI was made by dispersing the PANI in 1 M oxalic acid and stirring for 4 h. The oxalate doped PANI was filtered and washed with distilled water and dried in oven at $60 \text{ }^\circ\text{C}$ for 2 h.

Characterization of oxalate doped polyaniline pigment

FTIR analysis

The Fourier transform infrared spectroscopy (FTIR) spectra of oxalate doped PANI and PANI containing coated panels

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were recorded on NICOLET 380 FTIR spectrometer using ATR accessory at room temperature. In the case of coatings exposed to the corrosive media, localized FTIR measurements have been done with NICOLET 380 FTIR along with NICOLET CENTRAU μ S microscope.

X-ray diffraction analysis

X-ray diffraction pattern of the doped PANI were taken with Analytical X-ray diffractometer (Model PW 3040/60) using $CuK\alpha$ radiation in the 2θ range $0-90^\circ$ at the scan rate of 0.017° per minute.

Thermogravimetric analysis

The thermogravimetric analysis of oxalate doped PANI has been carried out using thermal analyzer (STA, 1500), Polymer laboratory, Thermal Science Ltd.

Preparation of paint with doped PANI and coated panels

The oxalate doped PANI containing paint was prepared using vinyl resin (supplied by Grand Polycos, India) Mwt. 30,000 with 1% by weight of PANI as pigment. Earlier studies [16] have shown that the coating containing 1% PANI has given corrosion protection as that of coating containing 3% PANI. The paint was prepared in such a way that it had the volume solids of 30–33%. The PANI pigmented paint was applied over sand-blasted (SA 2.5) mild steel (C 0.1%, Mn 0.46%, Si 0.074%, P 0.07%, S 0.028%) panels of size 15×10 cm. The dry film thickness

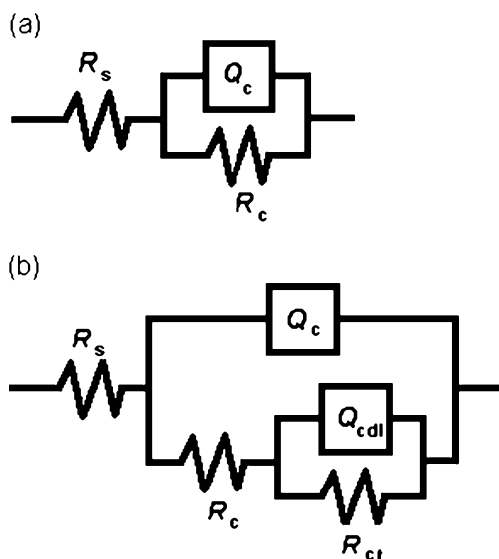


Fig. 1 Equivalent circuit for painted metals. **a** For intact coating. **b** For corrosion initiated coated panel

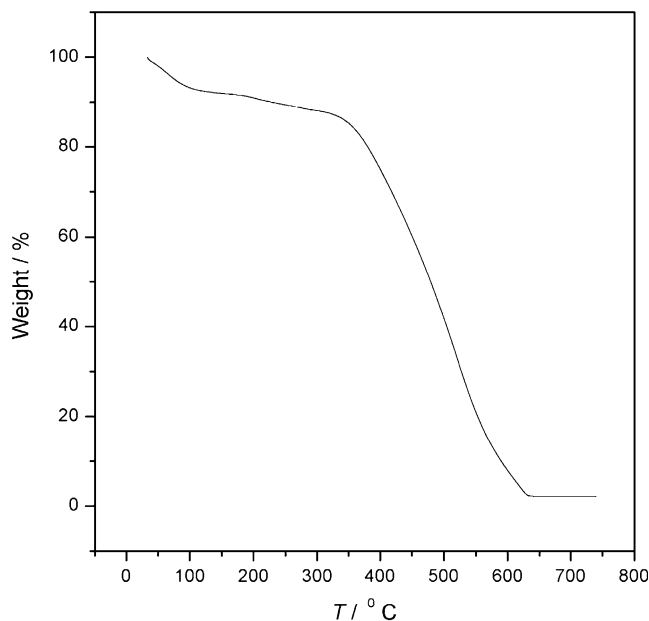


Fig. 2 Thermogravimetric analysis of oxalate doped polyaniline

of the coating was 50 ± 5 μ m. The coatings were evaluated after 10 days of curing at room temperature.

Evaluation of corrosion-resistant properties of the coating

Open-circuit potential measurements

A glass tube of 1.2 cm diameter was fixed on the coated steel panels with M-seal Adhesive. Solution of 3% NaCl was taken in the glass tube, and the saturated calomel reference electrode (SCE) was placed inside the glass tube. The open-circuit potential (OCP) of the coated steel was

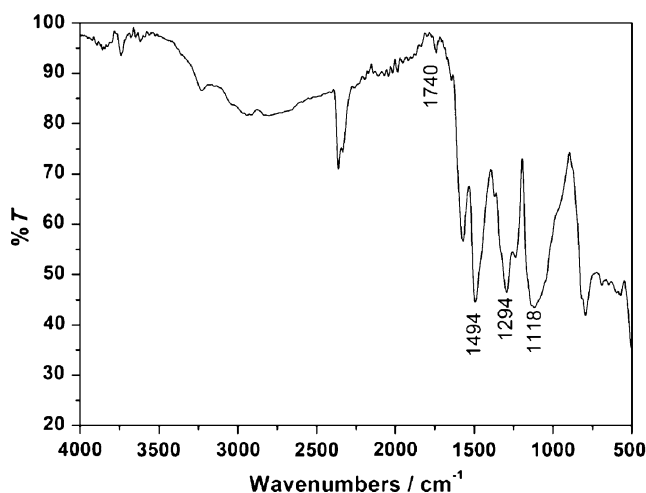


Fig. 3 FTIR spectra of oxalate doped PANI pigment

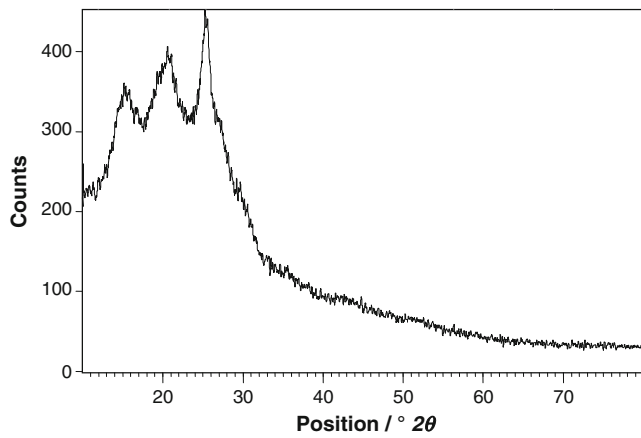


Fig. 4 XRD analysis of oxalate doped polyaniline

measured with respect to SCE using a high-input impedance voltmeter (HP 973 A).

EIS studies

The electrochemical cell as described above with a platinum auxiliary electrode inside the glass tube along with SCE reference electrode was used for EIS measurements. The assembly was connected to an Advanced Electrochemical System (PAR 2273). Impedance measurements were carried out using Powersine software for a frequency range of 100 kHz to 0.1 Hz with an AC signal of amplitude of 20 mV for different

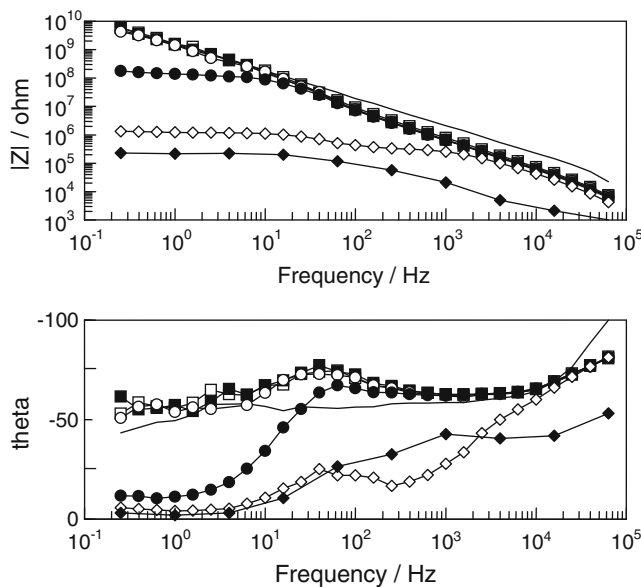


Fig. 5 Impedance plots of vinyl paint-coated steel in 0.1 M HCl. Solid line initial; black square 1 day; white square 4 days; black square 7 days; white circle 14 days; black circle 50 days; diamond 100 days

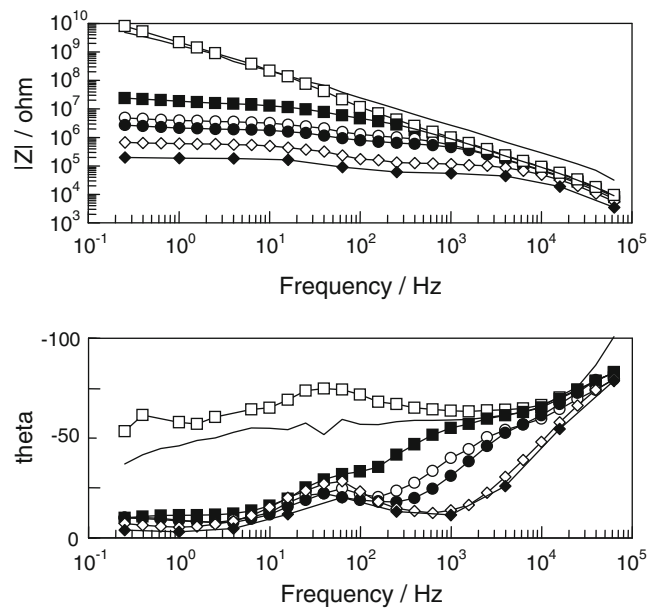


Fig. 6 Impedance plots of oxalate doped PANI containing vinyl paint-coated steel in 0.1 M HCl. Solid line initial; black square 1 day; white square 4 days; black square 7 days; white circle 14 days; black circle 50 days; diamond 100 days

immersion time in 3% NaCl. The impedance values are reproducible $\pm 2-3\%$. From the impedance plots, the coating resistance (R_c) and the coating capacitance (C_c) values were calculated using ZsimpWin 3.21 software using the equivalent circuit shown in Fig. 1a for the data with a single-time constant where R_s is the solution resistance, R_c is the coating resistance, and Q_c is the constant phase element (CPE) of the

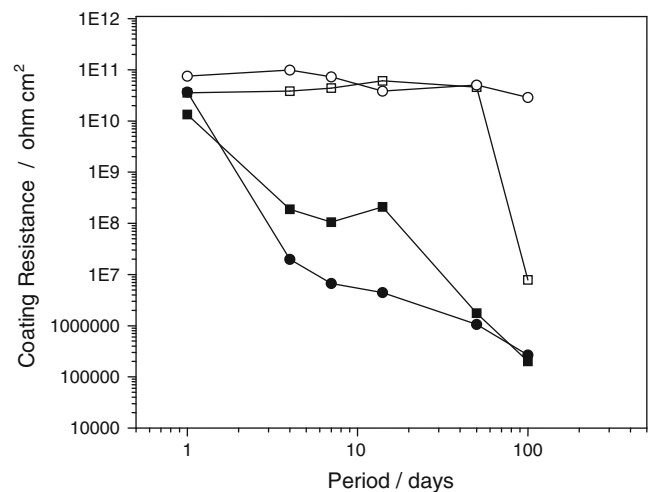


Fig. 7 Variation of coating resistance with immersion period. Black square vinyl coating in 0.1 M HCl; white square vinyl coating in 3% NaCl; black circle PANI incorporated vinyl coating in 0.1 M HCl; white circle PANI incorporated vinyl coating in 3% NaCl

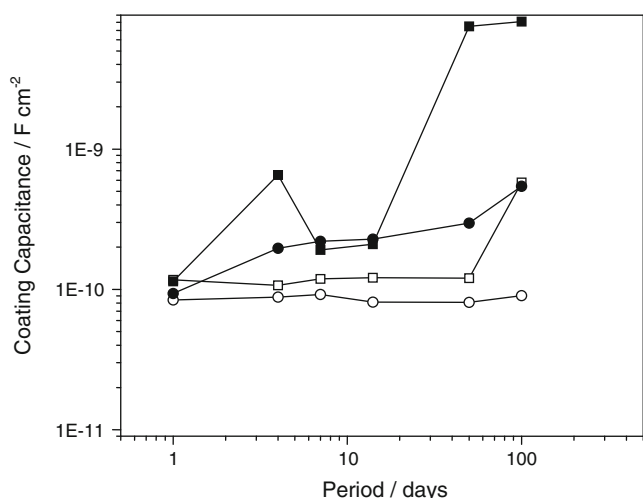


Fig. 8 Variation of coating capacitance with immersion period. *Black square* vinyl coating in 0.1 M HCl; *white square* vinyl coating in 3% NaCl; *black circle* PANI incorporated vinyl coating in 0.1 M HCl; *white circle* PANI incorporated vinyl coating in 3% NaCl

coating capacitance. In the case of impedance data with two time constants, the equivalent circuit as shown in Fig. 1b is used in which Q_{cdl} is the CPE of double-layer capacitance, and R_{ct} is the charge-transfer resistance.

For the description of a frequency-independent phase shift between an applied AC potential and its current response, a CPE is used which is defined in impedance representation as

$$Z(Q) = Y_0^{-1}(j\omega)^{-n} \quad (1)$$

where Y_0 is the CPE constant, ω is the angular frequency (in rad s^{-1}), $j^2 = -1$ is the imaginary number and n is the CPE

exponent ($n > 0$, for ideal capacitance $Z(\text{CPE}) = C$, $n = 1$). The following Eq. (2) is used to convert Y_0 into C_c [17],

$$C_c = Y_0 (\omega_m'')^{n-1} \quad (2)$$

where C_c is the coating capacitance and ω_m'' is the angular frequency at which “Z” is maximum. The above equation of Mansfeld et al. has been used in this study, since it has been shown to give capacitance values of coated samples with less error.

Results and discussion

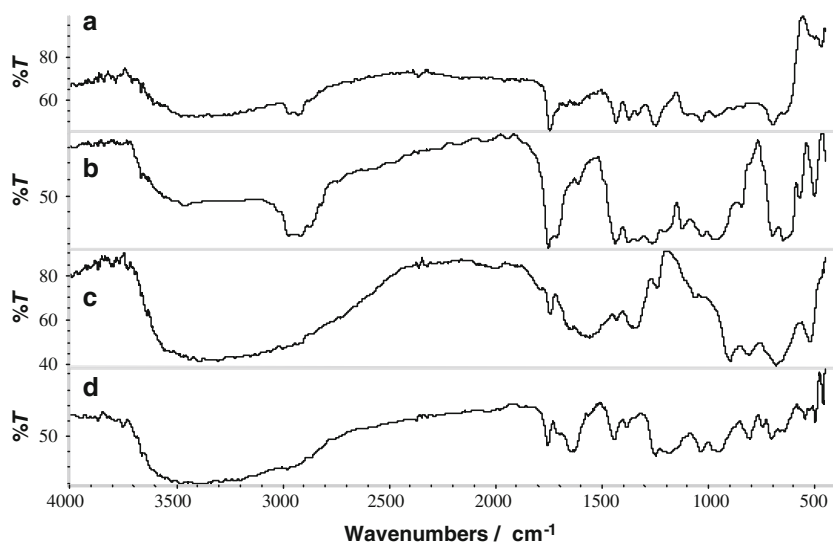
Thermogravimetric analysis

The thermogram of PANI–Oxalate is shown in Fig. 2. The first weight loss observed up to 83.32 °C, which is due to loss of water from PANI. The second stage of weight loss between 83.32 to 404 °C is due to removal of dopant molecules from the polymer [18]. The weight loss observed between 404 to 632 °C is due to the degradation of polymer chain. Similar results are reported by Erden et al [19].

FTIR studies

FTIR spectra of the oxalate doped PANI is shown in Fig. 3. The main peaks at 1,570, 1,494, 1,294, 1,118 cm^{-1} correspond to quinoid, benzenoid, C–N stretching of the secondary amine and the vibration mode of $-\text{NH}^+$ = structure [20, 21]. Besides, the band at 1,740 cm^{-1} is due to the carboxyl group of oxalate dopant [19]. These

Fig. 9 FTIR spectra of paint and surface beneath coating. **a** PANI containing vinyl paint-coated steel after exposure to 0.1 M HCl. **b** Surface beneath the PANI containing vinyl-coated steel after exposure to 0.1 M HCl for 100 days. **c** Oxalate doped PANI containing vinyl coating exposed to 3% NaCl. **d** Surface beneath the PANI containing vinyl-coated steel after exposure to 3% NaCl for 100 days



characteristic bands confirm that the oxalate doped PANI is of conducting state.

XRD studies

The X-ray diffraction (XRD) pattern of the PANI (Fig. 4) shows a peak at $2\theta=25^\circ$ revealing that the local crystallinity, which may be caused by the periodicity perpendicular to the polymer chain [22].

Evaluation of coatings

EIS studies of vinyl and PANI containing vinyl-coated steel exposed to 0.1 M HCl

The impedance spectra of vinyl-coated steel and PANI containing vinyl-coated steel are shown in Figs. 5 and 6. The coating resistance R_c and the coating capacitance values obtained from these spectra are shown in Figs. 7 and 8. In both the cases, it is found that the coating is able to offer protection up to 14 days, and after that, the resistance values are decreased below $10^6 \Omega \text{ cm}^2$. Besides, after 14 days immersion, the impedance behavior shows the occurrence of charge-transfer reaction due to iron dissolution by the existence of two time constants. The charge transfer resistance R_{ct} values for the coating without PANI are found to be 3.1×10^5 and $2.5 \times 10^3 \Omega \text{ cm}^2$, and for PANI containing coating, the values are 5.6×10^5 and $1.4 \times 10^5 \Omega \text{ cm}^2$ for 50 and 100 days of exposure, respectively. Even

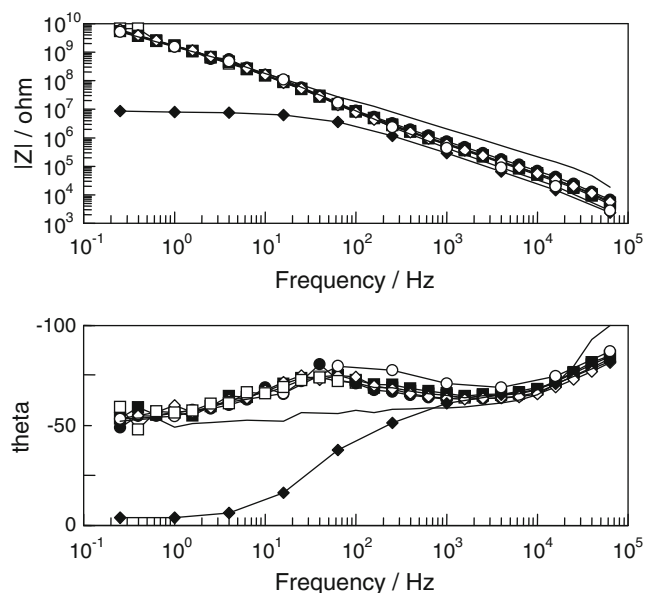


Fig. 10 Impedance plots of vinyl paint-coated steel in 3% NaCl. Solid line initial; black square 1 day; white square 4 days; black square 7 days; white circle 14 days; black circle 50 days; diamond 100 days

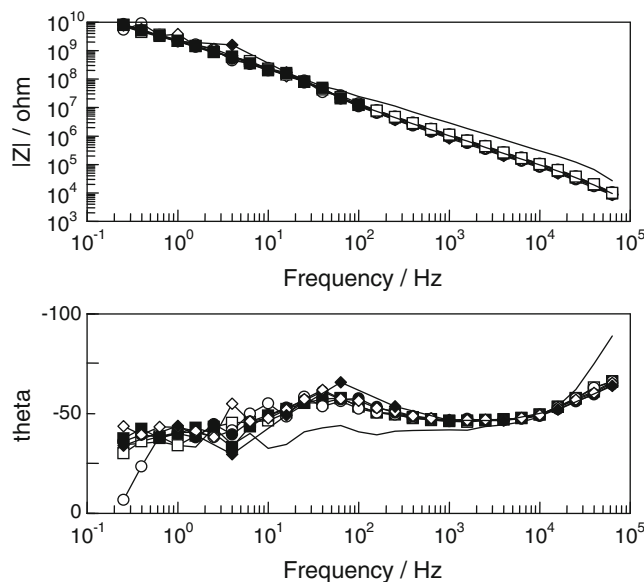


Fig. 11 Impedance plots of oxalate doped PANI containing vinyl paint-coated steel in 3% NaCl. Solid line initial; black square 1 day; white square 4 days; black square 7 days; white circle 14 days; black circle 50 days; diamond 100 days

though the coating resistances for coatings with and without PANI are same after 50 and 100 days of exposure, the high R_{ct} values for the coating with PANI indicate that the metal dissolution is less for steel coated with PANI containing coating. The coating capacitance values of PANI containing

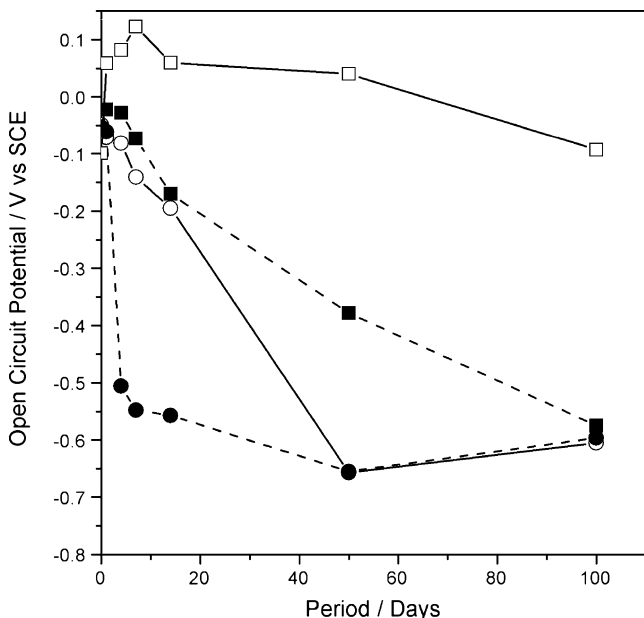


Fig. 12 OCP variation of coated panels. White circle blank in 0.1 M HCl; black square blank in 3% NaCl; white circle PANI in 0.1 M HCl; white square PANI in 3% NaCl

coating are found to be less than that of the coating without PANI.

Figure 9a shows the FTIR spectra of the coated steel after exposure to 0.1 M HCl. The presence of peak at $1,120\text{ cm}^{-1}$ indicates that the PANI is in conducting state [23, 24] even after exposure to 0.1 M HCl for 100 days. However, the intensity of the peak is decreased in comparison with that of PANI pigment. Figure 9b shows the FTIR spectra of the surface beneath the coating after exposure to 0.1 M HCl for 100 days. The presence of peak at $1,740\text{ cm}^{-1}$ indicates the presence of oxalate group and the presence of peaks of the PANI on the surface show the formation of iron–PANI–oxalate complex.

EIS studies of vinyl and PANI containing vinyl-coated steel in 3% NaCl

The impedance behavior of vinyl and PANI containing vinyl-coated steel in 3% NaCl is shown in Figs. 10 and 11. Figures 7 and 8 also give the variation of coating resistance and coating capacitance for different immersion periods. The coating resistance (R_c) values of the vinyl-coated steel in 3% NaCl are decreased to $7.83 \times 10^6 \Omega\text{ cm}^2$ after 100 days of immersion. But in the case of PANI containing vinyl-coated steel, the R_c values are remained at $10^{10} \Omega\text{ cm}^2$ even after 100 days of immersion in 3% NaCl solution. Besides the coating capacitance values of the PANI containing coating is found to be nearly one order less than that of coating without PANI. This shows that the PANI containing coating offers higher protection than that of the coating without PANI.

The FTIR spectra of the PANI containing vinyl-coated steel after exposure to 3% NaCl solution for 100 days are shown in Fig. 9c. It can be seen that the peak at $1,118\text{ cm}^{-1}$, which is due to doped state of PANI, is found to be absent in the case of coated steel after exposure to 3% NaCl solution after 100 days. This indicates that the state of PANI has changed from conducting to non-conducting form due to release of oxalate dopant ions. Besides, the formation of iron–PANI–dopant complex on the iron surface has been observed from the presence of peaks for oxalate and PANI in the FTIR spectra (Fig. 9d) on the surface where the coating has been removed after exposure to 3% NaCl solution for a period of 100 days. Recent ESCA studies [25] have confirmed the interaction between PANI and substrate.

OCP studies of coated steel

Figure 12 shows the variation of OCP values for coated steel in 0.1 M HCl and 3% NaCl solutions. It can be seen that PANI containing coatings exhibit noble potential values in 3% NaCl solution, while in acid media, the

potential values are remained in active range. Such type of shifts in OCP in noble direction by PANI pigmented coating on steel in NaCl solution have been reported earlier [2, 18, 26] and explained due to formation of passive layer underneath the film.

These studies have shown that oxalate doped PANI containing vinyl coatings are able to offer higher corrosion protection in NaCl solution due to redox property of PANI along with the formation of iron–PANI–dopant complex beneath the coating. Earlier studies by da Silva et al. [12–14] and Kamaraj et al. [15] and de Souza [26] have shown that the mechanism of protection of doped PANI containing coating is due to passivation of steel along with the iron–PANI–dopant complex formation.

Conclusions

The oxalate doped PANI containing coating is able to protect steel in neutral media since the impedance values are maintained at $10^{10} \Omega\text{ cm}^2$ even after 100 days exposure. The PANI containing coating protects steel in neutral media by forming passive oxide film on iron due to redox property of PANI along with the formation of iron–PANI–dopant complex formation.

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