

Effects of Polyaniline Content in Chlorrub-Based Coatings on Corrosion Protection of Steel

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ABSTRACT: Corrosion protection of steel coated with chlorrub resin containing polyaniline has been studied in 3% NaCl by electrochemical impedance spectroscopy (EIS). Polyaniline was prepared by oxidative polymerization of aniline using ammonium persulphate in HCl medium. Using the synthesized polyaniline, paints were prepared using chlorrub resin with 1, 3, and 5% polyaniline. The variation of resistance and capacitance of the coating with time

has been found out by EIS. The study has shown that the polyaniline content of 1% is able to offer sufficient protection of steel in neutral media and usage of higher percentage of polyaniline does not have beneficial effect. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3994–3999, 2006

Key words: polyaniline; corrosion; steel; neutral media; chlorrub

INTRODUCTION

Because of the environmental restrictions on the use of heavy metal and chromate containing coating, a new class of coating systems with conducting polymer such as polyaniline (PANI) have been developed in the recent years. The new class of primer coatings containing inherently conducting polymer have more tolerance to pin holes due to the passivating ability of the polymer pigment.^{1–4} After the first report by Mengoli et al.,⁵ several studies have been reported on the performance of polyaniline containing paint coating. Lu et al.⁶ found that the PANI-coated steel exhibited 100 times less corrosion rate in 0.1N HCl than that observed with epoxy paint alone. Fahlman et al.⁷ have shown that the partial coatings of PANI–Emeraldine base (PANI–EB) can protect iron even over a 15 mm distance of uncoated metal. Santos et al.⁸ have studied the corrosion resistant property of steel coated with polyaniline by spraying a 2% solution of polyaniline in *N*-methyl pyrrolidene. They found that steel coated with polyaniline has gained 100 mV in corrosion potential in 3% NaCl and showed a lower corrosion rate. Wei et al.⁹ have shown that the PANI–EB coated steel has performed well than that with other barrier coatings. Wessling and Posdorfer¹⁰ have studied the performance of polyaniline primer coating on steel by salt

spray test, impedance test, and scanning kelving probe in 3% NaCl, and have found that the coating system with PANI primer is highly corrosion resistant. Jain et al.¹¹ have investigated the mechanism of protection by doped conducting polymer. It is reported by Mc Andrew et al.¹² that the nonconducting polyaniline containing coating has performed well as corrosion resistant coating in 1M NaCl. Arango et al.¹³ have found that undoped polyaniline coating has got poor corrosion resistance due to poor adhesion. deSouza et al.¹⁴ have studied the performance of polyaniline acrylic blend with sulfonate dopant and shown that the blends form a passivating complex with the dopant anion along with the iron oxide passive layer. Dominis et al.¹⁵ and da Silva et al.¹⁶ have compared the performance of polyaniline primers with different dopants on the corrosion protection of steel and found that epoxy top coated system showed adequate corrosion protection up to 2 years in 3.5% NaCl solution and the performance depended on the nature of dopant. In a study,¹⁷ it is reported that the lower polyaniline loaded paint coating has been found to be more corrosion resistant. Kinlen et al.¹⁸ have shown that the phosphonic acid doped polyaniline containing coating has got superior corrosion resistance than that of sulfonic acid doped polyaniline coating. Wroblewski et al.¹⁹ have reported that the doped electrically conducting form of PANI film on steel with epoxy top coat gave excellent corrosion performance in 3.5% NaCl and 0.1M HCl even at scribed areas. Pud et al.²⁰ have studied the effect of neat PANI–EB salt and PANI–EB primers with epoxy top coats on the corrosion of mild steel in chloride solution. Coatings with PANI

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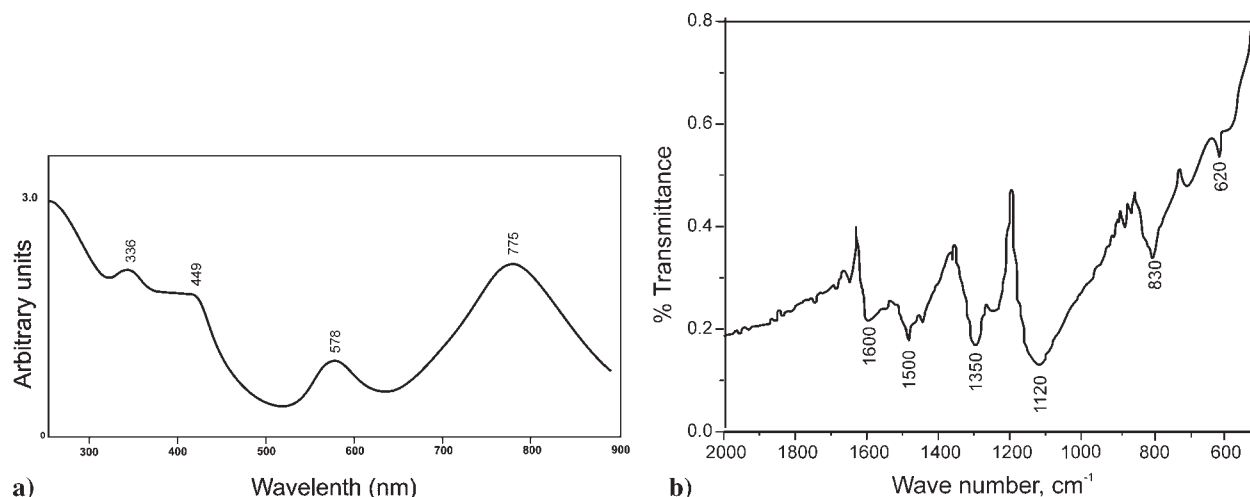


Figure 1 (a) UV-visible spectrum of poly(aniline); (b) FTIR spectra of PANI pigment.

primer were found to be highly corrosion resistant. Kinlen et al.²¹ have studied the corrosion performance of coating with PANI-ES in phenolic and acrylic binder with epoxy or polyurethane top coat on steel by salt spray test. They have compared the performance of PANI containing primer with conventional zinc containing primer. They have found that the samples with PANI primer are superior to zinc containing primer in terms of blister size, blister density, and scribe activity. In a recent study,²² it is reported that the polyaniline pigmented vinyl coating on steel is able to protect in 3% NaCl and 0.1N HCl solutions. The recent reviews²³⁻²⁵ summarize the research work on corrosion control of ferrous metals by conducting polymers and conducting polymer blended organic coatings. Most of the earlier studies have been devoted to establish the anticorrosive property of polyaniline in the organic coating. The aim of the present study is to find out the amount of polyaniline content in the organic coating on the corrosion protection ability of steel. Accordingly, a study has been made on the corrosion protection ability of steel by the presence of 1 to 5% polyaniline in the chlorrub-based coatings.

EXPERIMENTAL

The polyaniline pigment was prepared as per the procedure described earlier.²² PANI was obtained by oxidative polymerization of distilled aniline (Aldrich) in 1.0M HCl aqueous solution using ammonium persulfate (Merck) as oxidant. The green color powder obtained was filtered, washed thoroughly with distilled water, and dried in vacuum oven. The polyaniline was characterized by UV-visible and FTIR spectroscopy. The PANI was dissolved in *N*-methylene pyrrolidine (NMP) solution and the UV-vis spectra were recorded using HITACHI-U 3400 UV-vis spec-

trophotometer. FTIR spectra were recorded by PERKIN ELMER-PARAGON 500 using KBr pelleted PANI pigment. The particle size of polyaniline pigment was measured by HORBIA LA-910 Laser scattering particle size distribution analyzer and the conductivity of the compressed polyaniline pigment pellet measured by the four probe resistivity method. Chlorub (chlorub 10) was used as the base resin for PANI coating formulations. A base solution of chlorub was prepared by dissolving 50 g of chlorub in 100 g of xylene. The above-mentioned solution was plasticized with chlorinated paraffin in the ratio of 60 : 40. The polyaniline pigment in the range 1 to 5% was added to the above mixture. The paint was prepared using an attritor.

The paint containing polyaniline was coated on the pickled steel surface of size 10 × 15 cm². The thickness of the coating was ca. 100 ± 5 μm. After drying, a glass tube of 1.2 cm diameter with 3 cm length was fixed on the painted plate by m-seal adhesive. The test solution 3% NaCl was taken in a tube. The saturated calomel reference electrode and a platinum foil counter electrode were placed inside the solution. The cell setup was connected to electrochemical impedance analyzer (Model 6310, EG and G). Impedance measurements were carried out for a frequency range of 100 KHz-0.01 Hz with input amplitude of 20 mV.

RESULTS AND DISCUSSION

Characterization of PANI pigment

Figure 1(a) shows the UV spectra of PANI pigment. The adsorption peak of polyaniline at 336 nm shows the π - π^* transition in the benzenoid ring and 578 nm shows the donor-acceptor interaction of quinonoid ring. The well-known cation radicals and localized polaron peaks were observed at 449 and 775 nm.

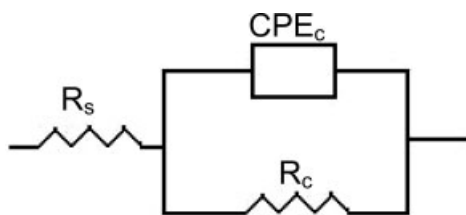
The Fourier transform infrared spectra of PANI pigment is shown in Figure 1(b). As shown in figure, the characteristic peaks of PANI occur around 1600, 1500, 1350, and 1120 cm^{-1} in agreement with the literature.²⁶ The peaks at 1500 and 1600 cm^{-1} are due to benzenoid and quinoid groups, respectively. The two strong peaks at 620 and 1120 cm^{-1} are due to out of plane and in plane C—H bending motion of quinoid and benzenoid rings, respectively. The peaks at 1250 and around 1350 cm^{-1} are characteristic amines. The peak at 830 cm^{-1} is due to the 1,4-*para*-substituted benzene ring. The band characteristic of the conducting protonated form is observed at 1250 cm^{-1} and interpreted as C—N⁺ stretching vibration in the polaron structure.²⁷

The particle size of polyaniline pigment was 3–5 μm and the conductivity of the compressed polyaniline pigment pellet was ca. 0.02 S cm^{-1} .

Performance evaluation of PANI pigmented coating

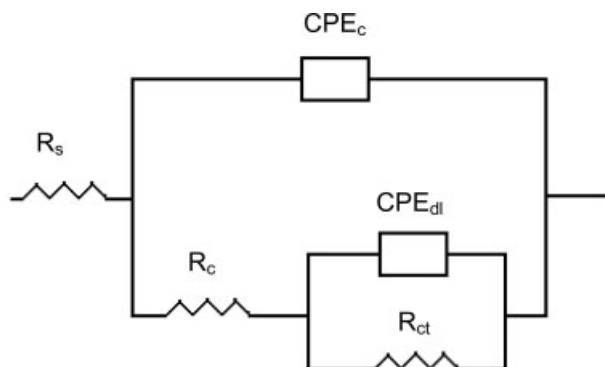
The corrosion performance of the coated steel with 1, 3, and 5% PANI has been evaluated by electrochemical impedance spectroscopy (EIS) for different periods of exposure in 3% NaCl solution.

Nyquist representations of the impedance data were analyzed with Zview software. When there is a single time constant, the impedance data were analyzed using the equivalent circuit



where R_s is the solution resistance, R_c is the coating resistance, and CPE_c is the constant phase element corresponding to the capacitance of the coating.

When there exists two-time constants, the impedance data were analyzed using the equivalent circuit



where CPE_{dl} is the constant phase element corresponding to the interfacial double layer capacitance, and R_{ct} is the charge transfer resistance due to the Faradaic reaction at the interface.

Assumption of a simple R–C is usually a poor approximation especially for systems showing depressed semicircle behavior in the impedance plots. The depressed semicircular behavior has been attributed to the heterogeneity of the solid metal surface.^{28,29} For the description of a frequency independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) is used, which is defined in impedance representation as

$$Z(\text{CPE}) = Y_0^{-1}(j\omega)^{-n}$$

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. Depending on n , CPE can represent resistance ($Z(\text{CPE}) = R$, $n = 0$), capacitance ($Z(\text{CPE}) = C$, $n = 1$), inductance ($Z(\text{CPE}) = L$, $n = -1$) or Warburg impedance for ($n = 0.5$).³⁰ The correct equation to convert Y_0 into C is,³¹

$$C = Y_0(\omega'_m)^{n-1}$$

where C is the coating capacitance (C_c) when considering the first semicircle, and C represents the double layer capacitance (C_{dl}) while considering the second semicircle, and ω'_m is the angular frequency at which Z'' is maximum.

Figures 2–4 show the impedance behavior of coated steel in 3% NaCl. The open circuit potential (OCP) variations and the impedance values are given in Tables I–III. In the case of coated steel with 1% PANI, the impedance diagrams showed a single time constant indicating the absence of Faradaic reaction. The open circuit potential values are stabilized around -600 mV versus SCE. There is not much gain in OCP values as observed in the case of PANI with vinyl coatings.²² However, the paint film resistance is decreased slightly after the 3rd day of immersion and started to increase steadily from 16.8 to 47.9 $\text{M } \Omega \text{ cm}^2$ with increased period of immersion. The coating capacitance initially increased from 8.91 $\times 10^{-9}$ to 1.8 $\times 10^{-9}$ F cm^{-2} and then remained constant around 4.8 $\times 10^{-9}$ F cm^{-2} . The high resistance value of the coating after 42 days of immersion indicates the protective nature of the coating. Besides, the impedance behavior does not indicate the occurrence of any Faradaic reaction.

The impedance diagrams for 3% PANI-containing coating show a two-time constant behavior after 15 days of immersion, which indicates the occurrence of Faradaic reaction. The open circuit potentials are

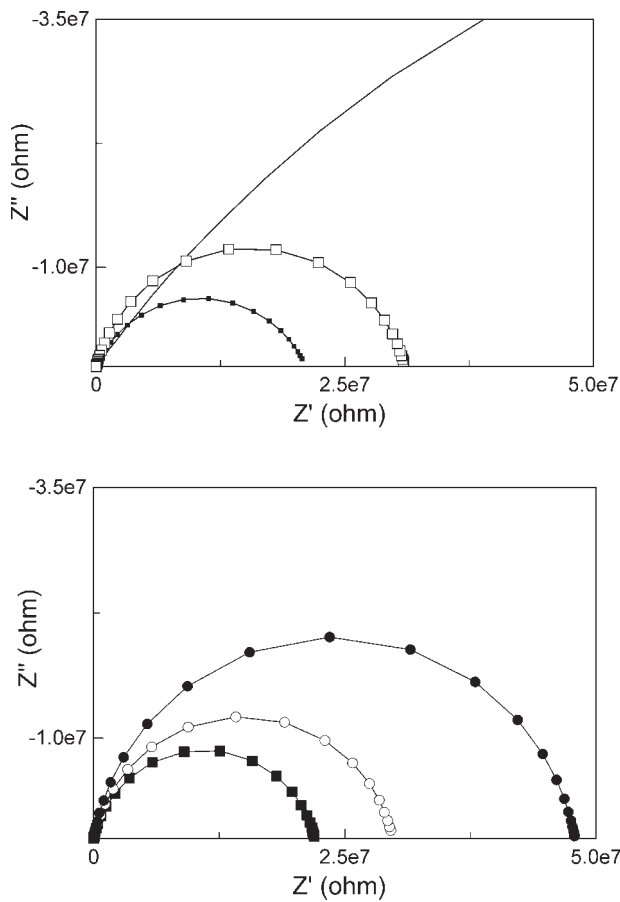


Figure 2 Impedance curves of chlrorub coating containing 1% PANI on steel in 3% NaCl—, Initial; ■, 1 day; □, 7 days; ■, 15 days; ○, 28 days; ●, 42 days.

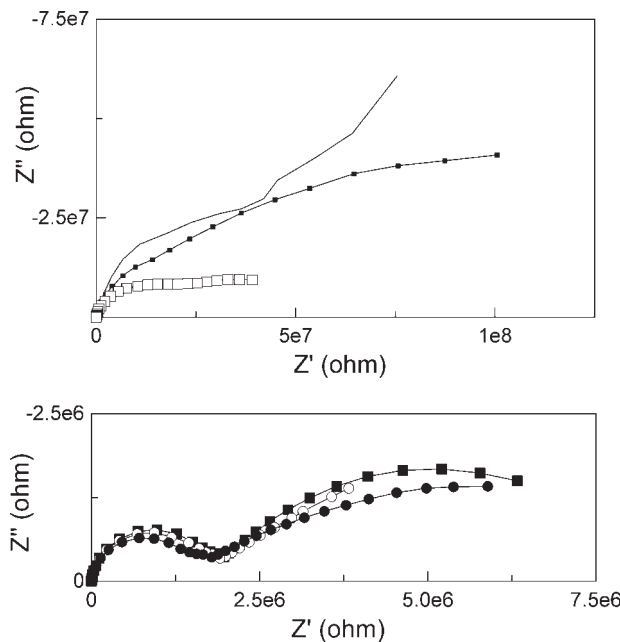


Figure 3 Impedance curves of chlrorub coating containing 3% PANI on steel in 3% NaCl—, Initial; ■, 1 day; □, 7 days; ■, 15 days; ○, 28 days; ●, 42 days.

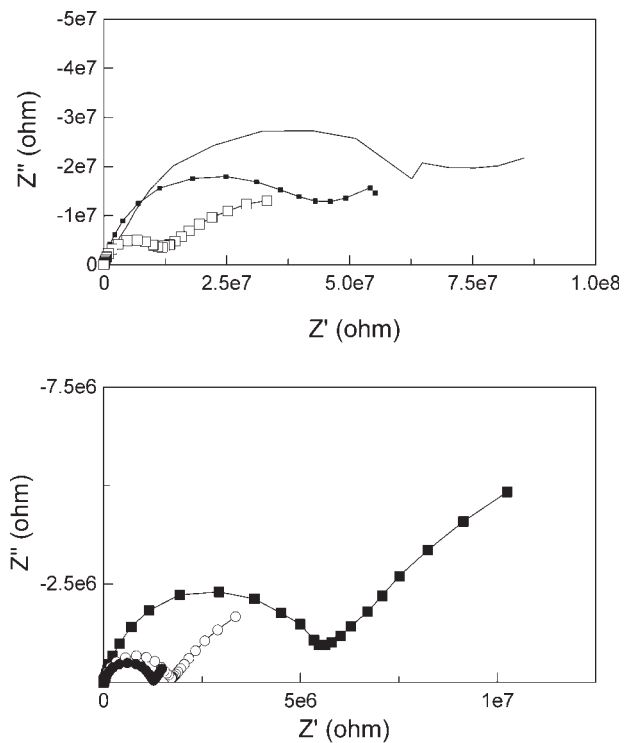


Figure 4 Impedance curves of chlrorub coating containing 5% PANI on steel in 3% NaCl—, Initial; ■, 1 day; □, 7 days; ■, 15 days; ○, 28 days; ●, 42 days.

stabilized around -0.620 mV versus SCE. The resistance of the coating has been found to be steadily decreasing with immersion time and reaches $2.0M \Omega \text{ cm}^2$ after 42 days of immersion. This value is 20 times less than that obtained for coating with 1% PANI. The coating capacitance values are in the range of 1.3 to $8.4 \times 10^{-10} \text{ F cm}^{-2}$. The charge transfer resistance values have been found to be decreased from 73.5 to $9.7M \Omega \text{ cm}^2$ in 42 days of immersion in 3% NaCl. Moreover, the double layer capacitance values are increased to $9.0 \times 10^{-7} \text{ F cm}^{-2}$ in 42 days immersion. These show the onset of small amount of iron dissolution reaction. The onset of iron dissolution is confirmed by the coloration of solution due to iron hydroxide.

TABLE I
Impedance Parameters of Chlrorub Coating Containing 1% PANI on Steel in 3% NaCl

Time (days)	OCP (mV vs. SCE)	$R_c (\Omega \text{ cm}^2)$	$C_c (\text{F cm}^{-2})$
Initial	-0.494	2.05×10^8	2.85×10^{-9}
1	-0.588	1.68×10^7	2.07×10^{-9}
2	-0.608	2.11×10^7	0.79×10^{-9}
3	-0.617	2.95×10^7	0.62×10^{-9}
7	-0.630	3.11×10^7	0.58×10^{-9}
15	-0.648	2.22×10^7	5.58×10^{-9}
28	-0.601	2.97×10^7	5.17×10^{-10}
42	-0.601	4.79×10^7	5.17×10^{-10}

TABLE II
Impedance Parameters of Chlorrub Coating Containing 3% PANI on Steel in 3% NaCl

Time (days)	OCP (mV vs. SCE)	Coating parameters		Faradaic parameters	
		R_c (Ω cm ²)	C_c (F cm ⁻²)	R_{ct} (Ω cm ²)	C_{dl} (F cm ⁻²)
Initial	-0.328	6.40×10^7	5.19×10^{-10}	-	-
1	-0.569	2.02×10^8	7.87×10^{-10}	-	-
2	-0.621	8.09×10^7	1.34×10^{-9}	-	-
3	-0.618	1.14×10^8	8.37×10^{-10}	-	-
7	-0.648	2.85×10^7	7.42×10^{-10}	-	-
15	-0.630	3.46×10^6	7.81×10^{-10}	7.35×10^7	2.45×10^{-8}
28	-0.623	2.44×10^6	6.86×10^{-10}	2.41×10^7	5.42×10^{-7}
42	-0.616	2.33×10^6	4.88×10^{-10}	9.65×10^6	9.0×10^{-7}

The impedance plots of coating with 5% PANI have showed two-time constant behavior after 7 days of immersion, indicating the onset of Faradaic reaction after 7 days of immersion. The resistance of the coating has decreased from 73 to $1.6M \Omega$ cm² after 42 days of immersion. On comparing the coating resistance of 1% PANI containing coating, this value is nearly 40 times less. The coating capacitance values are in the range of 1.3 to 6.8×10^{-10} F cm⁻². The charge transfer resistance value after 15 days of immersion is $89M \Omega$ cm² and this value is decreased to $1.1M \Omega$ cm². Besides, the C_{dl} value is increased to 3.3×10^{-6} from 3.3×10^{-7} F cm⁻² with time of immersion. This decrease in R_{ct} values shows the onset of iron dissolution reaction.

Comparing the impedance values of 1, 3, and 5% PANI containing coatings on steel in 3% NaCl, it is found that the coating with 1% PANI is more corrosion resistant than that of 3 and 5% PANI containing coating. The effect of PANI content on the corrosion protection of steel has been reported by Wang et al.,³² Plesu et al.,³³ and Samui et al.¹⁷ Wang et al.³² have studied the corrosion resistant property of epoxy coating containing 1.0, 1.2, and 2.0% PANI in 3% NaCl and found that the coating with 1% PANI was found to have good corrosion protection property. Plesu et al.³³ have studied the corrosion performance of acrylic coating with 5.6, 10.8, and 20.0% PANI with phosphorous anion in 3.5% NaCl. They have reported that the coating with 5.6% PANI with

phosphorous anion is found to be corrosion resistant. Samui et al.¹⁷ identified the effect of PANI hydrochloride pigment content with styrene butyl acetate resin on the corrosion protection of steel in 3.5% NaCl solution. They varied the PANI content from 0.1 to 20 parts. They found that the lower loading of PANI-HCl pigment was found to be more effective in corrosion protection when compared with that of the other. Further, it is found that the coating resistance of 1% PANI containing coating is increasing steadily after 1 day immersion due to passivation of iron by polyaniline pigment.^{8,10,18}

The role of polyaniline in coatings on the corrosion protection of steel has been reported by several investigations. Lu et al.⁶ have shown that the PANI films could protect the steel surface by the formation of layers of Fe₂O₃ and Fe₃O₄ and the passivation effect is due to the redox activity of polyaniline. Further, it is found that PANI forms an iron-PANI complex.³⁴ Both SEM and XPS studies have shown that an oxide layer has been formed between the PANI coating and the steel surface, and is composed mainly of Fe₂O₃ above a very thin Fe₃O₄ layer.²⁻⁴ Li et al.³⁵ have shown that PANI-containing primer coated steel has got higher charge transfer resistance than the coated steel without PANI due to the passivation effect of PANI.

Earlier studies^{15,16} on the role played by dopant ions on corrosion protection of steel by polyaniline by Dominis et al. and Silva et al. have shown that

TABLE III
Impedance Parameters of Chlorrub Coating Containing 5% PANI on Steel in 3% NaCl

Time (days)	OCP (mV vs. SCE)	Coating parameters		Faradaic parameters	
		R_c (Ω cm ²)	C_c (10^{-10}) (F cm ⁻²)	R_{ct} (10^7) (Ω cm ²)	C_{dl} (F cm ⁻²)
Initial	-0.617	7.30×10^7	4.19	-	-
1	-0.617	5.83×10^7	6.26	-	-
2	-0.609	5.03×10^7	6.01	-	-
3	-0.621	3.37×10^7	6.34	-	-
7	-0.635	2.14×10^7	6.84	8.97	3.84×10^{-10}
15	-0.602	7.08×10^6	5.52	3.02	3.33×10^{-7}
28	-0.590	1.69×10^6	1.56	2.01	1.26×10^{-6}
42	-0.626	1.14×10^6	1.34	1.04	3.3×10^{-6}

iron forms complex with dopant ions, which forms a secondary layer over and above the passive film formed by polyaniline. Hence, in the case of higher polyaniline containing coating, the polyaniline can release higher amounts of doped chloride ions, which can depassivate the passive layer formed by PANI. Hence, lower PANI content coating has been found to be more protective than that of higher PANI content coating.

CONCLUSIONS

EIS studies of chlorub-based coating on steel with 1, 3, and 5% polyaniline have shown that the coating with 1% polyaniline has got higher corrosion resistance. The resistance of coating with 1% PANI is found to be increasing with period of immersion in 3% NaCl due to passive film formation by polyaniline. Besides, coating with 1% PANI exhibits no iron dissolution reaction, whereas coating with 3 and 5% PANI have shown that the onset of iron dissolution reaction is due to increased release of doped chloride ions present in the polyaniline.

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