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Electropolymerised polyaniline films as effective replacement of carcinogenic chromate treatments for corrosion protection of aluminium alloys

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ABSTRACT

Owing to the carcinogenic nature of chromate coatings, alternate coatings with intrinsically conducting polymers such as polyaniline (PANI) and polypyrrole (Ppy) have been developed. Hence a study has been made on the effect of electropolymerised PANI films on corrosion protection performance of epoxy coating on AA 2024 and AA 7075 aluminium alloys. Polyaniline was electropolymerised on both the alloys by galvanostatic method. A post treatment of cecrium was given to seal the pinholes of PANI film. Epoxy coating was applied over these films and their corrosion protection performance was found out by EIS studies in 3% NaCl and salt spray test. EIS studies have shown that the coating resistance (R_c) of PANI with the epoxy coated aluminium alloys has remained above $10^6\ \Omega\,cm^2$ whereas the alloys coated with epoxy alone have shown the R_c values less than $10^4\ \Omega\,cm^2$. Besides, the salt spray tests showed a better corrosion protection of PANI with epoxy coated aluminium alloys.

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1. Introduction

Due to light weight and high strength properties, the aluminium alloys find immense applications in aerospace industries. Being a very reactive metal, aluminium forms a thin solid protecting film of oxide which prevents the further corrosion of the material while in contact with solutions containing complexing agents (i.e. halides), aluminium undergoes localized corrosion. Over the years various protection methods have been developed to prevent the degradation processes of aluminium and its alloys. Application of organic coating is a good old way of taking advantage of the mechanical property of the metal while protecting them from corrosion. Adhesion of these organic coatings on aluminium is very poor and needs some pretreatment like chromating. The most common pretreatment of aluminium alloys before painting is covering the metal substrate with chromate conversion coating in order to improve the adhesion of paint [1]. The chromium (VI) containing conversion coatings have been reported to be hazardous to the environment and human health. In this context, conducting polymers appeared to be a possible replacement for Cr (VI) based coatings [2–10]. Among the conducting polymers, polyaniline (PANI) is the most studied polymer in corrosion protection studies due to its easy synthesis and stability. Aqueous electrochemical polymerization is found to be an attractive process for the production of primer coating on metal, which will replace hazardous chromate pretreatment. The advantages of aqueous electropolymerisation are: (1) the aqueous solutions used are environmentally favorable, (2) the formation and deposition of polymer coating are simultaneous process which can be easily automated, (3) the production cost is relatively low and (4) the properties of the coatings can be controlled by varying the electrochemical parameters. Epstein et al. [11] have studied the corrosion protection ability of emeraldine base form of PANI for AA 3003 and AA 2024 T3 alloys and reported that these coatings were effective in reducing corrosion. Racicot et al. [12] have reported that PANI protects aluminium alloys by forming a passive layer. Tallman et al. [13] have shown that a PANI – epoxy two coat system on AA 2024 T3 alloy gave good corrosion protection. Vilca et al. [14] have studied the corrosion protection performance of electropolymerised PANI on AA 2024 T3 alloy. Cogan et al. [15] have reported the existence of galvanic couple between the base AA 2024 T3 alloy and the PANI coated alloy. Ogurtsov et al. [16] have studied the corrosion inhibition of AA 3003 alloy by coatings containing undoped PANI and PANI doped with sulfonic acid. Wang et al. [17,18] have studied the corrosion protection ability of electrodeposited PANI on AA 1100 alloy and found that PANI coatings offered protection against localized corrosion. Shah et al. [10,19] have studied the corrosion protection performance of electrodposited PANI and substituted PANI on AA 2024 alloy. Karpakam et al. [20] and Kamaraj et al. [21] have reported that electrodeposited polyaniline coatings on AA 2024 alloy and AA 7075 alloy are not much protective and a post treatment in cerium salt solution is necessary to improve the corrosion protection of inhomogeneous PANI coatings.

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In addition with PANI coatings. Rahmana et al. [22] have shown that pyrrole films are capable of working as primer for corrosion protection of carbon steel. Most of the earlier studies were mostly related to the corrosion protection performance of PANI coatings on aluminium alloys. For practical applications, not much data is available regarding the usage of electropolymerised PANI coating as primer which can replace either chromate conversion coating or chromate based primer coating in corrosion protection of aluminium alloy by organic coatings. Hence a study has been made on the effectiveness of electrodeposited PANI coating on the corrosion protection performance of AA 2024 and AA 7075 aluminium alloys by epoxy paint coatings.

2. Experimental

2.1. Electrodeposition of PANI on aluminium alloy

Aluminium AA 2024 and AA 7075 alloy sheets of 12 mm thick were procured from M/s Virat Aluminium, Mumbai. The alloys were cut into rectangular samples of size 8 × 4 cm and electropolymerisation was carried out by galvanostatic method from the respective baths at the appropriate conditions for an area of 7 × 4 cm. The pretreated AA 2024 and AA 7075 alloys were used as working electrodes, platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode.

2.1.1. Pretreatment of AA 2024 and AA 7075

The aluminium alloy samples were mechanically polished with 1/0, 2/0, 3/0 emery papers successively and then dipped in 5% NaOH solution for 2 min to activate the surface. After this stage, the samples were cleaned with cleaning powder to remove the black colored smudge formed over the surface and were washed thoroughly with running water and dipped in conc. HNO_3 solution for half a minute. The samples were then washed with distilled water and used for electropolymerisation.

2.1.2. Electropolymerisation of aniline on AA 2024 and AA 7075 alloy

The pre-treated AA 2024 and AA 7075 alloy samples were masked with adhesive tape to get an effective working area of 28 cm^2 at one of its ends. Electropolymerisation of aniline was carried out by galvanostatic polarization in which 20 mA cm^{-2} current was impressed for an hour on AA 2024 using the bath composition:

Oxalic acid:	0.5 M
Aniline:	0.12 M

Electropolymerisation on AA 7075 alloy was carried out by the same galvanostatic polarization condition from the following bath:

Oxalic acid:	1 M
Aniline:	0.5 M

For both the alloys, the thickness of electropolymerised PANI coating was found to be 10 ± 1 μm. The colour of the electropolymerised film is light green and gives good adherence to the top coat.

2.2. Top coating on PANI coated aluminium alloys

Epoxy resin (epoxy equivalent 500) of 30% volume solids was prepared by refluxing 30 gm of 6071 resin with 70 cm^3 of solvent mixture of xylene, methyl isobutyl ketone (MIBK) and butyl cellosolve. The paint was prepared in a lab attritor. The pigments (TiO_2, talc, silica, aluminium sterate) were pre mixed before mixing it with the resin solution. Mixed solvent as described above was used. The attritor was run for 45 min. The paint was transferred to an airtight container. The paint was mixed with polyamide hardener (amine value 210–230 mg KOH/gm) in the mix ratio of 7:3 and applied over the electropolymerised PANI layer by brush and allowed for curing for one week. Control specimens were also prepared where in the paint was applied over the aluminium alloys without PANI coating. The thickness of the epoxy coating was found to be 60 ± 5 μm.

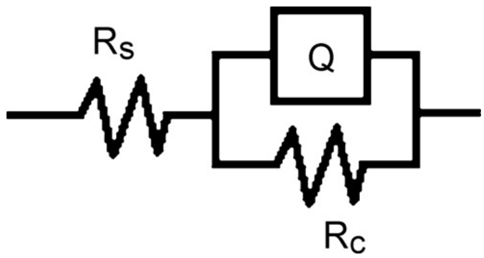

Fig. 1. Equivalent circuit for painted aluminium alloys.

2.3. Characterization of electropolymerised PANI layers by FTIR Spectroscopy

The FTIR spectra of electropolymerised polyaniline films on AA 2024 and AA 7075 alloys were recorded using NICOLET 380 FTIR spectrometer having ATR attachment at room temperature.

2.4. Corrosion protection evaluation of painted aluminium alloy samples

2.4.1. Salt spray tests

Painted aluminium alloy samples were exposed to salt spray as per *ASTM B117* wherein salt fog was created using 5% sodium chloride solution in the pH-6.5 to 7.2 range and the temperature of the exposure zone of the salt spray chamber is 35 ± 2 °C for 4 weeks.

2.4.2. EIS studies

For EIS studies, glass tubes of 1.3 cm diameter were fixed over painted (with and without electropolymerised PANI) aluminium alloy samples. 3% NaCl solution was poured into the glass tube as test medium. Platinum foil and saturated calomel electrode (SCE) were introduced into tube and this arrangement provides the conventional three-electrode setup for EIS measurements. The assembly was connected to an Advanced Electrochemical System (PARSTAT 2273). Impedance measurements were carried out using Powersine software in the frequency range of 100 kHz to 0.1 Hz with an AC signal of rms amplitude of 20 mV for different exposure time in 3% NaCl. The impedance values are reproducible up to ±2–3%. From the impedance plots, the solution resistance (Rs), 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. 1. 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

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

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 $Z(CPE) = C$, $n = 1$). The following Eq. (2) is used to convert Y_0 into C_c [23],

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

where C_c is the coating capacitance and ω_m'' is the angular frequency at which Z'' is maximum.

2.4.3. Open circuit potential (OCP) measurements

The experimental cell assembly as given above is used for OCP measurements. The open circuit potentials of the coated aluminium

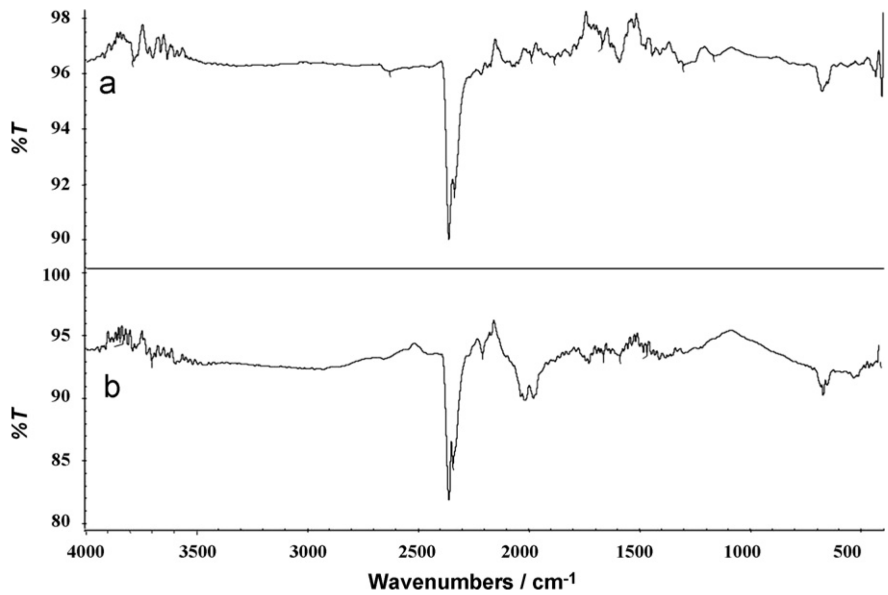

Fig. 2. FTIR spectra of electropolymerised polyaniline on AA 7075 (a) and AA2024 (b).

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

3. Results and discussion

3.1. Galvanostatic polarisation

The *E*–*t* transient curves shown elsewhere [21,24] obtained during the formation of polyaniline coatings on aluminium alloys for three different applied constant current densities viz. 15 mA, 20 mA and 25 mA have led to the following conclusions: The induction period during which metal dissolves decreases with increasing applied current densities. Passivation and polymerization potential values, on the other hand increase with increasing applied current density. Coatings of homogeneous appearance were obtained at 15–25 mA cm^{-2}. However, it has been found that the corrosion resistant properties of these electropolymerised PANI coatings in 3% NaCl has been increased very marginally when compared to the uncoated aluminium alloy. In some cases, acceleration of corrosion is also noticed due to the presence of micro pores in the electropolymerised PANI coating. Hence a post treatment for the electropolymerised coating is made to fill the pores. A cerium post treatment of PANI coated aluminium alloy samples in 1000 ppm of cerium salt solution for 30 min at 60 °C has been given to enhance the corrosion protection ability of electroploymerised PANI coatings over aluminium alloys [21,24]. It has been reported that cerium is found to be preferentially deposited over copper rich regions and reduced the oxygen reduction reaction and hence decreased the corrosion rate. As reported by the authors [24] and Hamdy et al. [25], direct treatment of cerium solution does not provide good corrosion protection for aluminium alloys. They [25] also confirmed the presence of localized corrosion even after a long cerium treatment. The mechanism of corrosion inhibition due to cerium depends on the incorporation of cerium ions through the pores of the Al oxide layer to block the active surface sites.

Hence for further studies, the aluminium alloy samples were given the electropolymerised PANI coatings at 20 mA cm^{-2} with cerium post treatment.

3.2. FTIR spectroscopy studies of PANI coatings

Fig. 2a and b show the IR spectra of for polyaniline deposited on AA 7075 and AA 2024 alloys respectively. There were no specific differences in bands between polyaniline on two different alloys. The peak at 812 cm^{-1} is characteristic of para-disubstituted aromatic rings indicating polymer formation. The bands at about 1160 and 550 cm^{-1} are assigned to the in-plane and out-of-plane C—H bending motions of the aromatic rings, respectively. A band appearing near 1260 cm^{-1} represents the C—N stretching vibration. The band at approximately 1640 cm^{-1} is due to the quinoid ring units. The band at about 1450 cm^{-1}, demonstrates the presence of benzenoid rings. The band located at 3450 cm^{-1} corresponds to the N—H stretching vibration. The peak at 1730 cm^{-1} is the C═O peak of dopant oxalate ions [21,24].

3.3. Evaluation of painted panels

3.3.1. Evaluation of painted AA 2024 aluminium alloy samples

After curing, the painted AA 2024 alloy samples were evaluated for their corrosion protection properties by salt spray tests and EIS studies.

3.3.1.1. Salt spray studies of painted AA 2024 alloy samples. Visual observation of epoxy coated AA 2024 alloy control specimens (without PANI) showed the formation of blisters in the paint within one week (Fig. 3a) exposure to salt fog whereas the samples having electropolymerised PANI coating with epoxy top coat were blister free even after 4 weeks of salt spray exposure (Fig. 3b).

3.3.1.2. EIS studies of painted AA 2024 alloy samples. Fig. 4 shows the bode representation of impedance behaviour of epoxy coated AA 2024 alloy (control) in 3% NaCl. The coating resistance (R_c) and the coating capacitance (C_c) values obtained from these figures are given in Table 1. It can be seen from the table that the R_c value of epoxy-coated specimen is decreased from the initial value of $4.45 \times 10^6\ \Omega\,cm^2$ to $4.42 \times 10^4\ \Omega\,cm^2$ over the exposure period of 75 days. The impedance behaviour AA 2024 alloy having electropolymerised PANI coating with epoxy top coat in 3% NaCl is shown in Fig. 5. The impedance parameters derived from these figures are also given in Table 1. It can be seen that the electropolymerised PANI coating with epoxy top coated samples

Fig. 3. Photograph of AA 2024 alloy after exposure to salt spray for 4 weeks. (a) Epoxy coated sample; (b) electropolymerised PANI with epoxy coating.

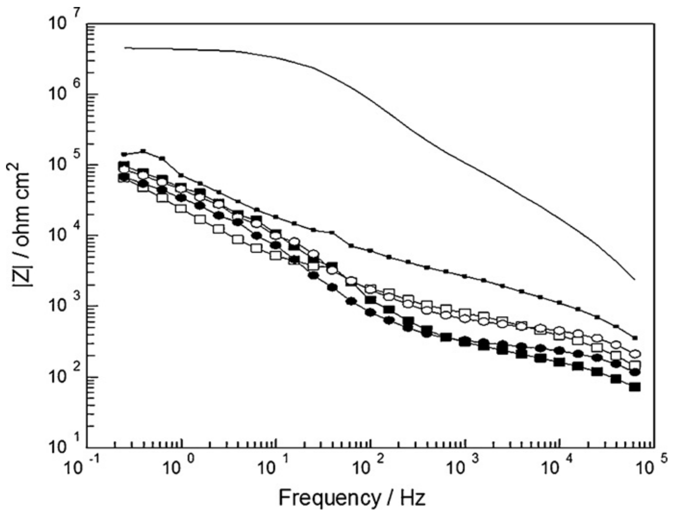

Fig. 4. Impedance behaviour of epoxy coated AA 2024 alloy in 3% NaCl. — initial; • 1 day; □ 7 days; ■ 25 days; ○ 50 days; ● 75 days.

Table 1
Impedance parameters of coated AA 2024 in 3% NaCl.

Time/days	Epoxy coating		Electropolymerised PANI with epoxy coating	
	R_c Ω cm^2	C_c F cm^{-2}	R_c Ω cm^2	C_c F cm^{-2}
Initial	4.45×10^6	2.24×10^{-9}	5.13×10^8	1.73×10^{-10}
1	6.80×10^5	8.99×10^{-8}	6.37×10^6	1.17×10^{-10}
7	6.43×10^4	3.13×10^{-6}	5.11×10^6	1.31×10^{-9}
25	1.52×10^4	3.36×10^{-6}	4.17×10^6	1.95×10^{-9}
50	1.60×10^4	4.75×10^{-6}	3.59×10^6	4.08×10^{-9}
75	4.42×10^4	4.37×10^{-6}	2.72×10^6	5.54×10^{-9}

have shown high coating resistance values, nearly two orders higher (5.13×10^8 Ω cm^2) than that of control sample. With continuous exposure to 3% NaCl solutions, the coating resistance is decreased to 2.72×10^6 Ω cm^2 after 75 days. Earlier studies by the authors [26] on the corrosion protection performance of strontium chromate pigmented primer paint along with top coat in NaCl solution for AA 2024 alloy have shown that the initial coating resistance and capacitance values are 7.28×10^8 Ω cm^2 and 8.27×10^{-11} F cm^{-2} and after 28 days exposure to NaCl solution, the resistance and capacitance values are found to be 1.69×10^6 Ω cm^2 and 1.5×10^{-10} F cm^{-2}. On comparing these values with that of electropolymerised PANI with topcoat, it is seen that the corrosion protection performance of electrodeposited PANI coating along with epoxy top coat is comparable with that of conventional strontium chromate based coating system.

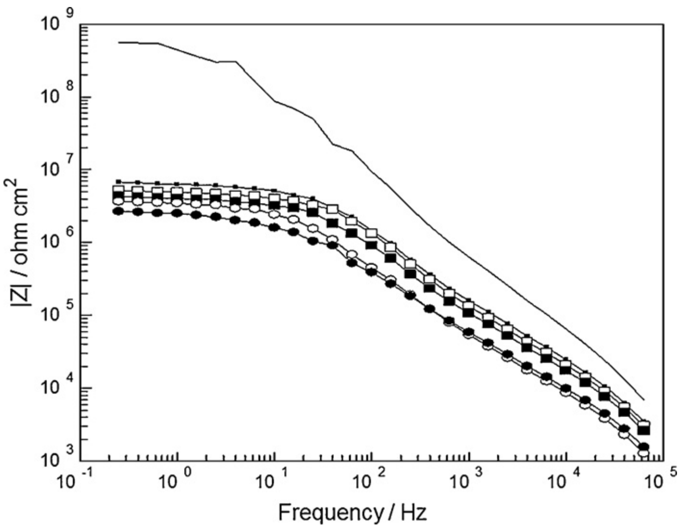

Fig. 5. Impedance behaviour of electropolymerised PANI with epoxy coated. AA 2024 alloy in 3% NaCl. — Initial; • 1 day; □ 7 days; ■ 25 days; ○ 50 days; ● 75 days.

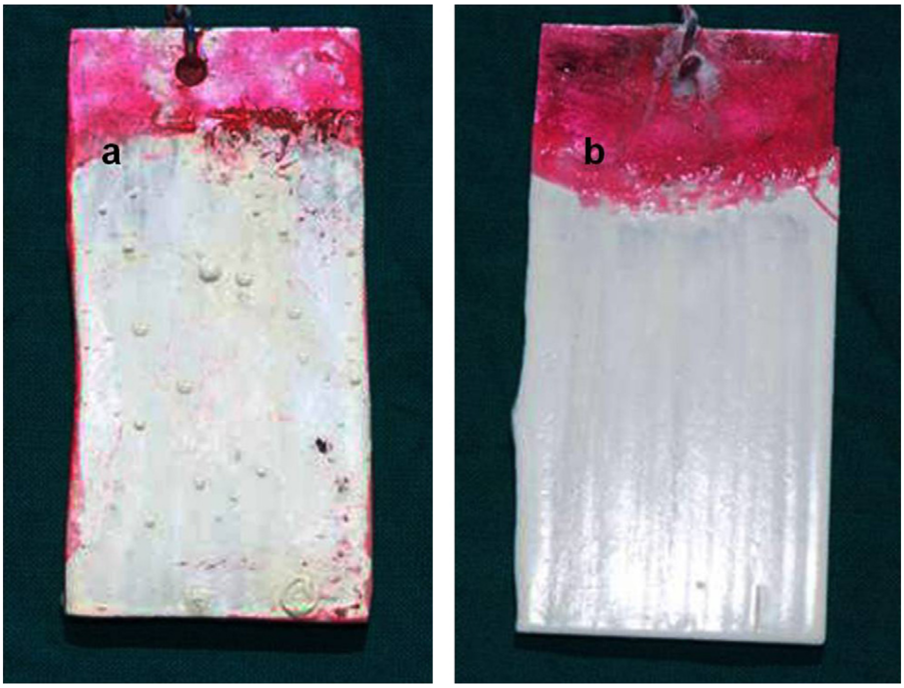

Fig. 6. Photograph of AA 7075 alloy after exposure to salt spray for 4 weeks. (a) Epoxy coated sample; (b) Electropolymerised PANI with epoxy coating.

3.3.2. Evaluation of painted AA 7075 aluminium alloy samples

After curing, the painted AA 7075 alloy samples were evaluated for their corrosion protection properties by salt spray tests and EIS studies.

3.3.2.1. Salt spray studies of painted AA 7075 alloy samples. Visual observation of AA 7075 alloy control specimens (without PANI) showed the formation of blisters in the paint in one week (Fig. 6a) whereas the electropolymerised PANI coating with epoxy top coated samples were blister free even after 4 weeks of salt spray exposure (Fig. 6b).

3.3.2.2. EIS studies of painted AA 7075 alloy samples. The coating resistance (R_c) and the coating capacitance (C_c) values obtained from the bode representation of impedance behaviour of painted AA 7075 alloy sample (without electropolymerised PANI) in 3% NaCl (Fig. 7) are given in Table 2. It can be seen from the Table 2 that the R_c value of control specimen is decreased from the initial value of 2.82×10^4 cm^2 to $1.77 \times 10^4\ \Omega$ cm^2 over the period of 75 days exposure. The impedance behaviour AA 7075 alloy having electropolymerised PANI coating with epoxy topcoat in 3% NaCl (as shown in Fig. 8), shows better corrosion protection than that of PANI free painted sample. The impedance parameters derived from these figures are also given in Table 2. As in the case of AA 2024 alloy, it can be seen that the electropolymerised PANI coated AA 7075 alloy with epoxy top coat exhibits better corrosion protection (nearly two orders). The initial value of coating resistance is $6.02 \times 10^8\ \Omega$ cm^2 which decreased to $7.99 \times 10^6\ \Omega$ cm^2 after 75 days of immersion in 3% NaCl.

Both salt spray tests and impedance tests have shown that the electropolymerised PANI coatings have increased the protective ability of epoxy coating on aluminium alloy samples. These studies have shown that the electropolymerised PANI coating can be a good alternative to chromate based coating for aluminium alloys.

The enhancement of passive oxide film formation by PANI has been confirmed from the open circuit potential (OCP) behavior of coated aluminium alloys. Fig. 9 shows the variation of OCP with immersion time for the epoxy alone coated and PANI with epoxy coated aluminium alloys in 3% NaCl. It can be seen that the epoxy coated aluminium alloys show the potential values of −0.780 V and −0.890 V for AA 2024 and AA 7075 aluminium alloys after 100 days immersion while that of PANI with epoxy coated aluminium alloy

Table 2
Impedance parameters of coated AA 7075 in 3% NaCl.

Time/Days	Epoxy coating		Electropolymerised PANI with epoxy coating	
	R_c Ω cm^2	C_c F cm^{-2}	R_c Ω cm^2	C_c F cm^{-2}
Initial	2.82×10^4	2.24×10^{-6}	6.02×10^8	1.41×10^{-10}
1	2.59×10^4	6.21×10^{-6}	1.74×10^8	3.55×10^{-10}
7	2.79×10^4	4.94×10^{-5}	9.38×10^7	4.85×10^{-10}
25	2.35×10^4	2.51×10^{-5}	1.09×10^7	1.17×10^{-10}
50	2.38×10^4	4.07×10^{-5}	8.49×10^6	7.33×10^{-10}
75	1.77×10^4	7.35×10^{-5}	7.99×10^6	1.10×10^{-9}

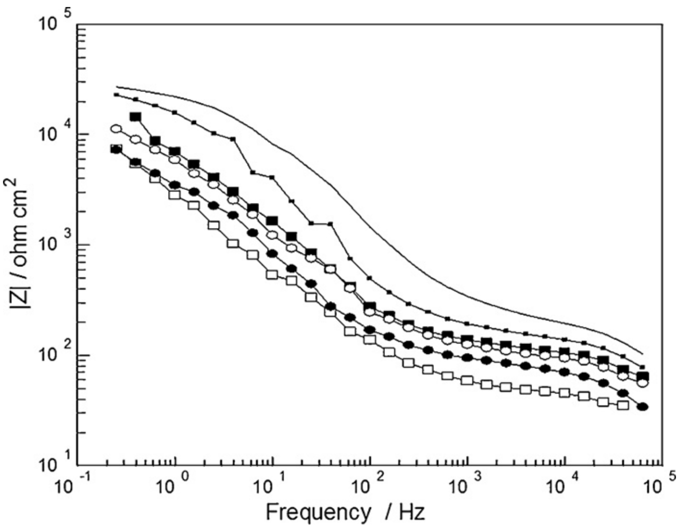

Fig. 7. Impedance behaviour of epoxy coated AA 7075 alloy in 3% NaCl. —Initial; • 1 day; □ 7 days; ■ 25 days; ○ 50 days; ● 75 days.

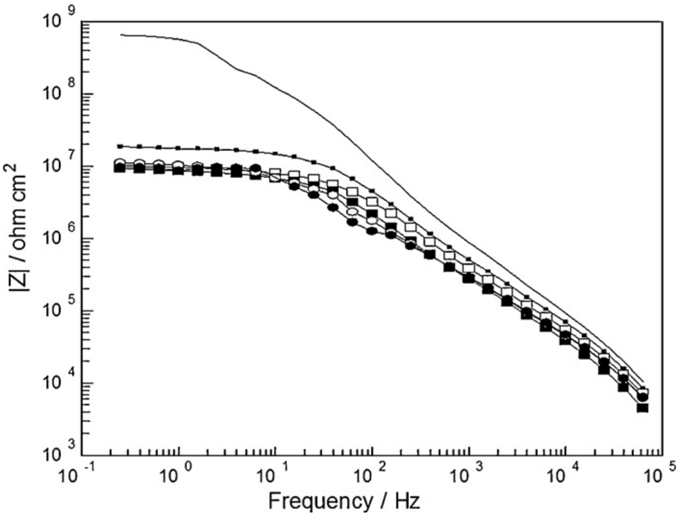

Fig. 8. Impedance behaviour of electropolymerised PANI with epoxy coated AA 7075 alloy in 3% NaCl. — Initial; • 1 day; □ 7 days; ■ 25 days; ○ 50 days; ● 75 days.

samples show the potential values of −0.288 V and −0.383 V for AA 2024 and AA 7075 alloys respectively. The positive shift of potential values of PANI with epoxy coated aluminium alloys indicates that PANI coating has enhanced passivation of aluminium by behaving as an effective cathode [17].

The present results agree with the observation of Shah and Iroh [10] who have shown that the AA 2024 alloy samples coated with polyaniline and epoxy top coat have shown no blister until 500 h of immersion test where as the coatings of epoxy alone have developed blisters after 96 h. Further, the electrodeposited polymer film has been found to increase the adhesion of paint coating by 50%. Besides, Tallman et al. [13] have reported that the polyaniline coated AA 2024 aluminium alloy with an epoxy top coat under immersion in dilute Harrison solution (0.35% $(NH_4)_2SO_4$ and 0.05% NaCl) has exhibited improved corrosion protection performance compared to an epoxy top coat alone. Similarly, Yang et al. [27] have observed that PANI with epoxy top coated AA 2024 aluminium alloy has shown improved filiform corrosion resistance in sea water as compared to epoxy coating.

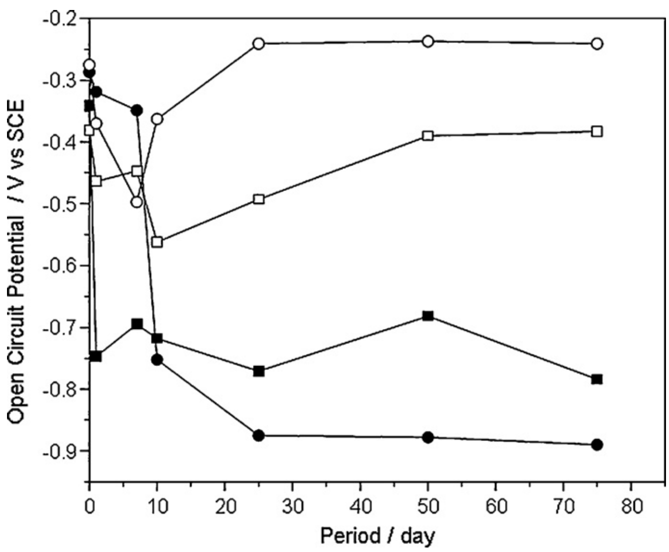

Fig. 9. Variation of open circuit potential of coated aluminium alloy samples in 3% NaCl. ■ AA 2024 alloy with epoxy coating; □ AA 2024 alloy electropolymerised PANI with epoxy coating; ● AA 7075 alloy with epoxy coating; ○ AA 7075 alloy electropolymerised PANI with epoxy coating.

The improved corrosion protection performance of polyaniline with epoxy top coating is mainly due to reactive interaction of polyaniline since the electrochemical potential of polyaniline (0.3 V vs. SCE) is sufficiently anodic to oxidize aluminium (E_{corr} of −0.7 V vs. SCE). Due to this, corrosion resistant passive oxide layer is formed between conducting polymer and the aluminium surface [27]. Besides, Racicot et al. [12] have shown that the corrosion protection performance of polyaniline coating is comparable to that of chromate conversion coating on aluminium surface.

4. Conclusions

The electrodeposition of polyaniline on AA 2024 and AA 7075 alloy samples was carried out by galvanostatic method from oxalic acid bath containing aniline. FTIR studies have shown that the polyaniline coating contains both benzenoid and quinoid groups and doped with oxalate ions. The influence of PANI coatings on aluminium alloy samples on the corrosion protection performance of epoxy coating has been found out by salt spray and EIS tests. The salt spray tests have shown that the aluminium alloy samples with PANI coating along with epoxy coating have been found to be blister free even after 4 weeks of salt spray exposure while the aluminium alloy samples with epoxy coating alone have developed blisters within a week. Besides, the EIS studies have shown that the coating resistance of the aluminium alloy samples coated with PANI along with epoxy coating has been found to be higher in comparison to that of aluminium alloy samples coated with epoxy coating alone.

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