Electropolymerised polyaniline films on AA 7075 alloy and its corrosion protection performance

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Abstract
Polyaniline has been electrodeposited on AA 7075 alloy and its corrosion protection ability has been studied by Tafel and impedance techniques in 1% NaCl. Pure polyaniline film is not found to protect the aluminium alloy due to galvanic interaction of polyaniline and aluminium surface exposed through pinholes and cracks. However, it is found that the corrosion resistance property of the polyaniline film can be substantially increased by post-treatment in cerium salt solution.

1. Introduction
Aluminium, a very reactive metal, forms a thin solid protecting film of oxide which prevents the further corrosion of the material. However, in contact with solutions containing complexing agents (i.e. halides), aluminium undergoes localized corrosion. Due to lightweight and high strength properties the aluminium alloys find application in aerospace industries. Over the years various protection methods have been developed to prevent the degradation processes of the aluminium and its alloys. Application of organic coating is a good way of taking advantage of the mechanical property of the metal while protecting them from corrosion. Adhesion of these organic coatings on aluminum is very poor and needs some pretreatment like chromating. The chromate coatings are formed by immersion of clean substrate in an acid or alkaline solution containing hexavalent chromium Cr (VI), which provide corrosion protection [1]. The carcinogenic nature of chromate conversion coatings forces an alternative method and there is a high demand for an environmentally friendly surface treatment.

Aqueous electropolymerization has been found to be an attractive process for the production of primer coating on metal, which will replace the chromate pretreatment. The advantages of aqueous electropolymerisation are: (1) the aqueous solutions used are environmentally favorable, (2) the technique combines the formation of polymer and deposition of coating in one process and this process 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. The electrodeposition of conducting polymers onto active metals has been a subject of great number of studies due principally to the corrosion protection properties of these coatings. A successful electropolymorisation requires the formation of a passive layer, which might be able to inhibit the dissolution of the oxidisable metal without blocking the access of the monomer and its further oxidation. Polyaniline and its derivatives and polypyrrole have been widely investigated because the low potential for polymer formation, easy preparation and stability of the formed films [1–10].

Electrodeposition of conducting polymer coatings on aluminum is difficult due to the existence of adherent naturally formed Al2O3. Husler and Beck [4] have reported that both polypyrrole film and a porous type Al2O3 form on a pre-treated aluminum from an aqueous solution containing oxalic acid and pyrrole. It is also reported that the pretreatments are essential for successful formation of both films (porous Al2O3 and Ppy film in the pores). Beck and Husler [5] also reported the formation of a similar type of Al2O3/Ppy composite using some non-aqueous media such as acetonitrile and methanol. Cheung et al. [6] confirmed the formation of a Ppy film on a thin Al2O3 film in a propylene carbonate solution. Saidman [7] studied the effect of pH on the electrochemical polymerization of pyrrole on aluminum and confirmed that electropolymorisation occurs at pH 12 under potentiostatic conditions. He also suggested that the nucle-
2. Experimental

Aluminum AA 7075 T6 alloy of 6 in. diameter rod was procured from M/s Virat Aluminium, Mumbai. Samples of 1 cm × 10 cm were cut from the rod after making slices of 1 cm thick. Oxalic acid, aniline, cerium chloride and sodium chloride used in this study for electropolymerisation, post-treatment and evaluations were of AR grade chemicals. Electrochemical measurements were made using Solartron electrochemical system (Model 1280 B). Pre-treated AA 7075 alloy was used as working electrode in the conventional three electrode assembly having platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode.

2.1. Pretreatment of AA 7075

The aluminum alloy was 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. HNO₃ solution for 30 s. The samples were then washed with distilled water and used for electropolymerisation.

2.2. Electropolymerisation on AA 7075

The pre-treated AA 7075 samples were masked with adhesive tape to get an effective working area of 1 cm² at one of its end. Electropolymerisation was carried out by galvanostatic polymerisation from the oxalic acid–based bath of the following composition, oxalic acid: 1 M and aniline: 0.5 M

2.2.1. Galvanostatic polarization

Electropolymerisation of aniline over AA 7075 surface was carried out by impressing a fixed current for a fixed duration of time. In this regard, current densities viz. 15 and 20 mA were applied and the corresponding potential transients were recorded for a period of 1 h.

2.3. Characterization of electropolymerised layers

2.3.1. FTIR spectroscopy

The FTIR spectra of electropolymerised polyaniline over AA 7075 was obtained using Smart Orbit ATR accessory along with NICOLET 380 FTIR instrument.

2.3.2. Morphology studies

The morphology of the electropolymerised coatings was analysed using Hitachi (Model S3000 H) scanning electron microscope.

2.3.3. Film thickness measurements

The thickness of the electropolymerised polyaniline coating on AA 7075 was measured using Elcometer thickness meter and it was found to be 10 μm.

2.3.4. Corrosion resistant property evaluation

The AA 7075 samples with electropolymerised polyaniline coating were evaluated for their corrosion resistance property in aerated 1% NaCl by Tafel polarization and electrochemical impedance spectroscopy using Solartron 1280B electrochemical analyzer.

In the case of Tafel polarization, the scanning of potential was done from −0.2 V vs. OCP to +0.2 V vs. OCP at a scan rate of 1 mV/s. From this anodic and cathodic polarization curves, the Tafel regions
were identified and extrapolated to $E_{\text{corr}}$ to get corrosion potential $i_{\text{corr}}$ using the Corr View software.

In the case of electrochemical impedance spectroscopy, a.c. signals of 20 mV amplitude and various frequencies from 10 kHz to 0.01 Hz at open circuit potentials were impressed to the coated aluminium alloys. From the impedance plots, the charge transfer resistance ($R_{\text{ct}}$) and the double layer capacitance ($C_{\text{dl}}$) values were calculated using ZsimpWin 3.21 software using the equivalent circuit.

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

where $Y_0$ is the CPE constant, $\omega$ 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 equation is used to convert $Y_0$ into $C_{\text{dl}}$ [21]:

$$C_{\text{dl}} = Y_0(\omega''_m)^n$$

where $C_{\text{dl}}$ is the double layer capacitance and $\omega''_m$ is the angular frequency at which $Z''$ is maximum.

The impedance data were analysed by using simple Randel's circuit, since one semi-circle is obtained in the Nyquist plot. Since polyaniline coating is conducting in nature, the resistance of the coating is negligible and the impedance behavior represents the charge transfer process of the aluminium alloy dissolution. From the measured charge transfer resistance value, the protection efficiency of the coating has been obtained from the relationship,

$$\text{Protection efficiency} (\%) = \frac{R_{\text{ct(C)}} - R_{\text{ct}}}{R_{\text{ct(C)}}} \times 100$$

where $R_{\text{ct(C)}}$ and $R_{\text{ct}}$ are the charge transfer resistance values in the presence and absence of polyaniline coating. From the Tafel polarization studies, the protection efficiency was obtained from the following equation:

$$\text{Protection efficiency} (\%) = \frac{i_{\text{cor}} - i_{\text{cor(c)}}}{i_{\text{cor}}} \times 100$$

where $i_{\text{cor}}$ and $i_{\text{cor(c)}}$ are the corrosion current density values in the absence and presence of polyaniline coating.

3. Results and discussion

3.1. FTIR spectroscopy

Fig. 1 shows the FTIR spectra of electropolymerised layer on aluminium alloy by galvanostatic polarization. The bands around 1725, 1650, 1497 cm$^{-1}$ correspond to C=O of oxalate and quinoid and benzenoid rings of polyaniline. It is found that the polyaniline film formed by galvanostatic conditions is having both benzenoid and quinoid moieties.

3.2. Surface morphology studies

The scanning electron micrograph of electropolymerised polyaniline coating over AA 7075 alloy by galvanostatic condition is shown in Fig. 2. The figure shows the presence of polyaniline coating with numerous cracks.

3.3. Corrosion protection evaluation of PANI film

Fig. 3 shows the typical potential transient for a galvanostatic pulse of 15 and 20 mA. The films were formed at these current densities for 1 h and were evaluated for their corrosion protection in 1% NaCl. These transients show an induction period for the coating formation over aluminium alloy. The induction period is decreased at higher applied current densities. Passivation and polymerization potential values, on the other hand are increased with increasing applied current density. Coatings of homogeneous appearance were obtained for studied current densities.

Fig. 4 shows the effect of air ageing in the Nyquist representation of complex impedance of the electropolymerised polyaniline on AA 7075 alloy in 1% NaCl under the galvanostatic conditions of 15 mA for 1 h. The charge transfer resistance ($R_{\text{ct}}$) and double layer capacitance ($C_{\text{dl}}$) obtained from these curves are given in Table 1.
Table 1

<table>
<thead>
<tr>
<th>Ageing period (day(s))</th>
<th>Impedance method</th>
<th>Polarization method</th>
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<tr>
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<td>Solution resistance, $R_s$ ($\Omega$ cm$^2$)</td>
<td>Charge transfer resistance, $R_{ct}$ ($\Omega$ cm$^2$)</td>
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is clearly seen from the table that the $R_{ct}$ values are decreased by the presence of coatings at all periods of air ageing. This decrease in $R_{ct}$ values may be attributed to localized attack of aluminium surface exposed through cracks by galvanic action of polyaniline coating. Besides the $C_{dl}$ values are found to be increased which indicates the occurrence of corrosion reaction.

Fig. 5 shows the polarization behavior of galvanostatically electropolymerized polyaniline coated on AA 7075 alloy at 15 mA for 1 h in 1% NaCl. The corresponding potentiodynamic polarization behavior is shown in Fig. 7. The $R_{ct}$, $C_{dl}$ and $i_{corr}$ obtained from these figures for different air ageing periods up to 4 days are presented in Table 2. The $R_{ct}$ values showed a decrease at the initial periods compared to that of blank. After 3 days of air ageing, the $R_{ct}$ values showed a slight increase resulting in corrosion protection. This increase in $R_{ct}$ values may be due to the oxidation of aluminium alloy at the localized cracks by the polyaniline coating. The results obtained from polarization method also confirmed the slight improvement in corrosion protection performance of this coating after prolonged air ageing.
Table 2
Kinetic parameters of electropolymerised polyaniline on AA 7075 alloy in 1% NaCl under the galvanostatic conditions at 20 mA for 1 h

<table>
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Corrosion studies of electropolymerised coating and also the SEM observation clearly have indicated the formation of a cracked polyaniline film on aluminium surface which cannot provide adequate corrosion protection as such. Hence, it is necessary to have a post-treatment which can seal the cracked areas where the bare aluminium is exposed to the aggressive environment. It has been reported that cerium ions are found to be preferentially deposited over copper rich regions and reduce the oxygen reduction reaction and hence decrease the corrosion rate [22,23]. University of Missouri-Rolla (UMR) has examined the use of cerium-based inhibitors in conversion coatings and primers [24–27]. In addition, rare-earths are generally considered non-toxic. Pioneering research by Hinton et al. found that cerium-based coatings were an environmentally benign alternative to chromate conversion coatings [28,29]. Recent work by Forsyth and co-workers has investigated the coupling of a rare earth metallic element with a multi-functional organic component to produce an inhibitor system that displays synergistic effects between the two components [30]. Hence a post-treatment in 1000 ppm cerium chloride solution at 60 °C has been made for the polyaniline coated aluminium alloys and the corrosion protection performance was studied.

Fig. 8 shows the impedance behavior of cerium treated galvanostatically electropolymerised coating at 15 mA for a duration of 1 h in 1% NaCl. Table 3 depicts the $R_{ct}$ and $C_{dl}$ values obtained from these curves showing enormous improvement of the corrosion resistant property of the coating due to cerium post-treatment. The $R_{ct}$ value is increased to 5508 Ω cm² from that of 2624 Ω cm² corresponding to the uncoated bare aluminium alloy having 52% protection efficiency. The corrosion current density (Table 3) obtained from the corresponding polarization curves (Fig. 9) for similar coatings also showed a greater decrease in its values from the blank value of 37 to 13 µA/cm².

The cerium treatment given to electropolymerised coatings formed at 20 mA for 1 h on AA 7075 also yielded beneficial results when evaluated by impedance method in 1% NaCl as shown in Fig. 10. The $R_{ct}$ values increased to 10618 Ω cm² accounting to 75% protection efficiency which with air ageing for 4 days increased to 16840 Ω cm² corresponding to 84% (Table 4). Besides, the $C_{dl}$ values are found to be decreased in the presence of polyaniline film. The $i_{corr}$ values obtained from the corresponding polarization curves are shown in Fig. 11 also indicated a decrease in its value to 3.8 µA/cm² confirming the enhanced corrosion protection ability of the cerium treatment. However, the corrosion protec-
Table 3
Effect of cerium post-treatment on the electropolymerised polyaniline on AA 7075 alloy in 1% NaCl under the galvanostatic conditions at 15 mA for 1 h

<table>
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</table>

Fig. 10. Effect of cerium post-treatment on the impedance behavior of electropolymerised polyaniline coated on AA 7075 alloy at 20 mA for 1 h in 1% NaCl. (—) Blank; (□) 1 day; (■) 2 days; (●) 3 days; (●) 4 days.

Fig. 11. Effect of cerium treatment on the polarization curves for uncoated and electropolymerised polyaniline coated on AA 7075 at 20 mA for 1 h in 1% NaCl. (—) Blank; (□) 1 day; (■) 2 days; (○) 3 days; (●) 4 days.

This study shows that the polyaniline film does not offer any significant corrosion protection of AA 7075 alloy. Similar observation has been reported for AA 2024 alloy [31], high purity aluminium [16,32] and 1100 aluminium alloy [33,34]. The main reason for poor corrosion protection performance of polyaniline films is attributed to the galvanic interaction between the polyaniline and the aluminium which accelerated the corrosion of aluminium. However, treatment in cerium salt solution plugs the pinholes and cracks of the polyaniline film and thereby enhances the corrosion protection ability of polyaniline film.

The sealing of pores in the PANI film on aluminium alloy by post-treatment in CeCl₃ solution is confirmed from the FTIR spectra of cerium salt solution treated PANI (Fig. 12). On comparing with the FTIR spectra of the PANI coated aluminium (Fig. 1), the peaks present in the region 600–400 cm⁻¹ which are due to the aluminium oxide [35,36] are absent in the cerium salt solution treated PANI film. The formation of cerium coatings on the cathodic precipitates has been confirmed by Aballe et al. [37,38].

It has been established that cerium affects the oxygen reduction reaction through cathodic inhibition via the formation of an oxide layer on the intermetallics of aluminium alloys [39–42]. This...
conclusion is also supported from the cathodic polarization studies (Figs. 9 and 11) after cerium treatment. It has been found that the oxygen reduction current values are found to be less for cerium treated samples in comparison to that of untreated samples.

4. Conclusion

Electropolymerisation of aniline on AA 7075 T6 alloy was obtained from oxalic acid bath by galvanostatic polarization (20 and 15 mA) for 1 h. FTIR spectroscopy studies revealed the presence of both benzenoid and quinoid structures confirming the presence of partially oxidized polyaniline (Emeraldine salt) which is known for its conducting nature. Surface morphological studies showed the coating with numerous surface cracks. Evaluation of these coatings in 1% NaCl by electrochemical impedance spectroscopy and potentiodynamic polarization revealed poor corrosion resistant behavior due to galvanic action of polyaniline. Cerium post-treatment for the polyaniline coatings on AA 7075 T6 alloys exhibited very high corrosion protection performance due to decreased rate of oxygen reduction reaction by forming cerium oxide coating on the pinholes in corrosive media containing chloride anions.

Acknowledgements

The authors thank the Director, Central Electrochemical Research Institute, Karaikudi for the support. They also thank D.R.D.O, New Delhi for the financial support.

References