

# Polyaniline Coated on Aluminum (Al-2024-T3): Characterization and Electrochemical Studies

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**ABSTRACT:** A polyaniline coating was deposited onto an Al-2024-T3 substrate using oxalic acid as electrolyte. Both galvanostatic and potentiostatic techniques were used to deposit polyaniline on aluminum under aqueous conditions. The dc polarization studies showed that polyaniline coatings reduced the corrosion rate of Al-2024-T3 significantly by about threefold compared to that of the control. The passivation of the polyaniline-coated aluminum was characterized by reflection absorption infrared spectroscopy and cyclic voltametry. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1669–1675, 2002

**Key words:** polyaniline; electrodeposition; cyclic voltammetry; aluminum alloy; corrosion protection

## INTRODUCTION

Corrosion of metals has been a persisting problem in society and, hence, it is an important area of research. Chromate conversion coatings are effective inhibitors of corrosion, but because of their toxic nature the international antipollution regulation may restrict their use in the near future.<sup>1</sup> In the past decade there has been a tremendous interest in finding a replacement for chromating processes. Conductive polymeric coatings of polyaniline and polypyrrole are some of the possible alternatives. This is because these polymers are chemically stable, environmentally viable, and have good corrosion resistance.

The high-strength aluminum alloy Al-2024-T3 is far more susceptible to corrosion attack than pure aluminum because it contains 4–5% copper. The presence of copper in the aluminum alloy introduces a galvanic couple between aluminum and copper, which accelerates corrosion. The mechanism proposed for corrosion protection of

copper-containing aluminum alloys is through removal of copper from the surface of the corroding alloy.<sup>2</sup> By coating or surface treatment we can inhibit corrosion in these high-strength aluminum alloys.

Although studies of corrosion protection of aluminum by conducting polymers have started only fairly recently,<sup>3–7</sup> the study of the protection of steel from corrosion has been conducted for some time.<sup>8–17</sup> These studies propose a strong interaction between the conducting polymer and a surface of steel. In practice, the corrosion protection is accomplished in one of the following ways: (1) cathodic protection, that is, the charge ( $e^-$ ) is donated from the sacrificing material to steel; (2) anodic protection, that is, the charge is withdrawn from steel; and (3) the steel surface is sealed off from corrosive attacks by a surface layer of another material, commonly a metal oxide.<sup>18</sup>

The earlier studies show that doped polyaniline improves the corrosion resistance of steel and iron.<sup>19,20</sup> The mechanism of corrosion protection of steel by a conducting polymer like polyaniline is believed to be the result of the formation of a thin oxide layer on the substrate and by chemical

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interaction between the polymer and the metal surface.

In this study we present the results of our studies of the corrosion-protection performance of polyaniline-coated Al-2024-T3. Techniques such as linear polarization, cyclic voltametry, galvanostatic, and reflection absorption infrared spectroscopy were used in this study.

## EXPERIMENTAL

All the chemicals used in this study were purchased from Aldrich Chemical (Milwaukee, WI). The aqueous solutions were prepared by using deionized water. Bare Al-2024 samples were purchased from Q-PANEL Inc. and polished with a 0.1- $\mu\text{m}$  microdiamond compound (Leco) on microcloth (Buehler). The samples were ultrasonically cleaned with acetone for 30 min and wiped with Kimwipes before electrodeposition.

### Galvanostatic Polymerization

Aqueous electropolymerization was carried out using a single-compartment polypropylene electrochemical cell. Polyaniline was deposited onto Al-2024-T3 using this cell. The Al-2024-T3 sample ( $1 \times 4 \times 0.063$  in.) was used as the working electrode. Two stainless steel plates ( $1.4 \times 5.75$  in.) were used as the counter electrodes and a saturated calomel electrode was used as the reference electrode. The saturated calomel electrode was purchased from Corning (Corning, NY). An aqueous solution of 0.3M oxalic acid and 0.1M aniline was used as electrolyte. An EG&G Electro-Optics/Princeton Applied Research (Salem, MA) 363 potentiostat/galvanostat was used as the power supply. Current densities ranging from 2 to 8 mA/cm<sup>2</sup> were used. Electrochemical polymerization was followed by tracing the potential versus time plot. The volume of electrolyte used for each experiment was 200 mL and the area of the electrode coated was 41.65 cm<sup>2</sup>. The reaction time was varied from 5 to 15 min. After the reaction the samples were rinsed with methanol and dried in an oven at 100°C for 1 h.

### Cyclic Voltametry

The counter, working, and reference electrodes were the same as was used for galvanostatic polymerization. An EG&G 273A potentiostat/galvanostat was used as the power supply. The cyclic

voltametry (CV) measurements were carried out at a scan rate of 20 mV/s for 1, 5, and 25 cycles. The scan range varied from  $-1.0$  to  $+3.0$  V versus SCE. The CVs were carried out by using oxalic acid (0.3M) as electrolyte and an aqueous solution of aniline (0.1M) and oxalic acid (0.3M), respectively. The same volume of electrolyte was used and the coated area was 41.65 cm<sup>2</sup>. The samples were rinsed and dried under conditions similar to those for samples obtained by galvanostatic polymerization.

### Dc Polarization Studies

An EG&G 363 potentiostat/galvanostat was used as the power supply. The same cell and electrodes were used as in galvanostatic polymerization. An Ag/AgCl reference electrode was used. An aqueous solution of 0.2M oxalic acid and 0.1M aniline was used as electrolyte. The current densities ranged from 2 to 6 mA/cm<sup>2</sup> and the reaction time ranged from 5 to 15 min. The samples were dried at 100°C for 1 h.

A flat cell (EG&G) was used for dc polarization measurements. A 3.5 wt % NaCl solution was prepared. Two measurements were taken on each face of the substrate and an average of four values is reported in this study. The corrosion current ( $I_{\text{corr}}$ ), corrosion potential ( $E_{\text{corr}}$ ), and corrosion rate were measured using EG&G 273A potentiostat equipped with a 352 soft corr III corrosion software.

The corrosion current is calculated using the Steary-Geary equation,

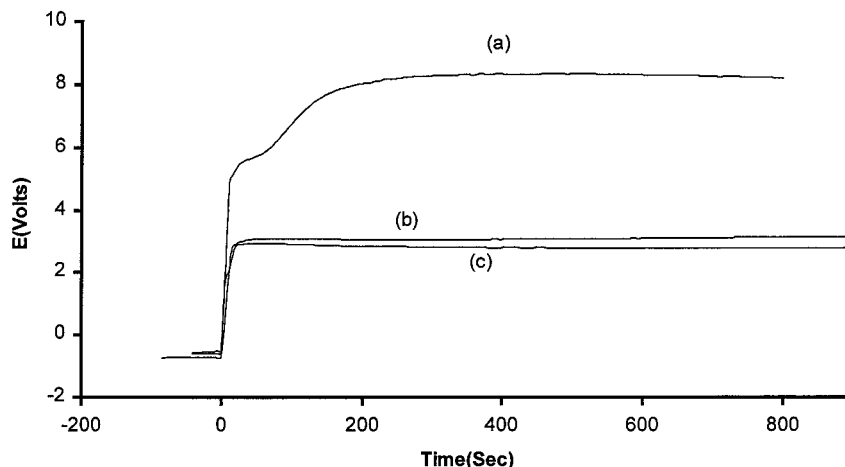
$$I(E) = I_{\text{corr}} [10^{(E-E_{\text{corr}})/\beta_a} - 10^{(E_{\text{corr}}-E)/\beta_c}]$$

where  $I$  is the total current at a potential  $E$ ,  $E_{\text{corr}}$  is the open circuit potential, and  $\beta_a$  and  $\beta_c$  are the Tafel proportionality constants for the anodic and cathodic reactions, respectively.

The corrosion rate is calculated using the following equation:

$$\text{Corrosion rate} = C(EW/d)(I_{\text{corr}}/A)$$

where  $C$  is the conversion constant ( $=3.268 \times 10^3$  when  $I_{\text{corr}}$  is expressed in amps and the corrosion rate in mmpy),  $EW$  is the equivalent weight of the sample in g,  $A$  is the area of the sample in cm<sup>2</sup>, and  $d$  is the density of the sample in g/mL.



**Figure 1**  $E-t$  traces for deposition of polyaniline on Al-2024. (a) Aqueous solution of 0.1M aniline and 0.3M oxalic acid; current density, 8 mA/cm<sup>2</sup>; (b) aqueous solution of 0.1M aniline and 0.3M oxalic acid; current density, 2 mA/cm<sup>2</sup>; (c) aqueous solution of 0.3M oxalic acid; current density, 2 mA/cm<sup>2</sup>.

### Characterization

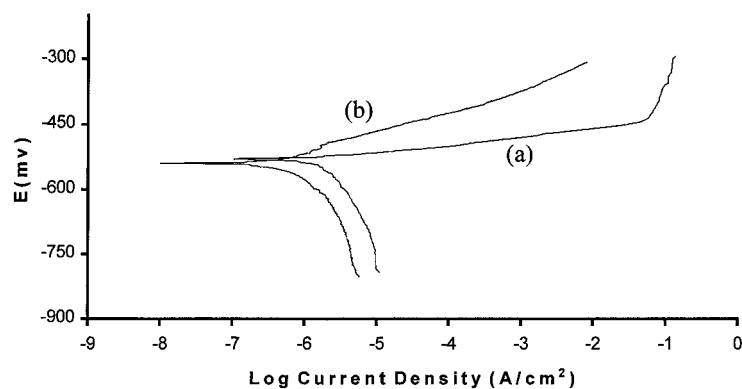
Reflection absorption infrared spectroscopy (RAIR) was carried out using a Bio-Rad FTS-40 FTIR spectrometer (Bio-Rad, Richmond, CA). The angular specular reflectance attachment was set to an incident angle of 50° and a resolution of 8 cm<sup>-1</sup> was used. A total of 600 scans were taken for each sample. A background spectrum of polished, bare Al-2024-T3 was subtracted from the acquired spectra. The samples used were the same samples that were prepared for the dc polarization measurements. An aluminum oxide and aluminum hydroxide coatings were formed by keeping bare Al-2024-T3 samples in boiling water for 1 h. An oxalate layer was also deposited

onto the bare Al-2024-T3 by keeping it in an oxalic acid solution for 6 h.

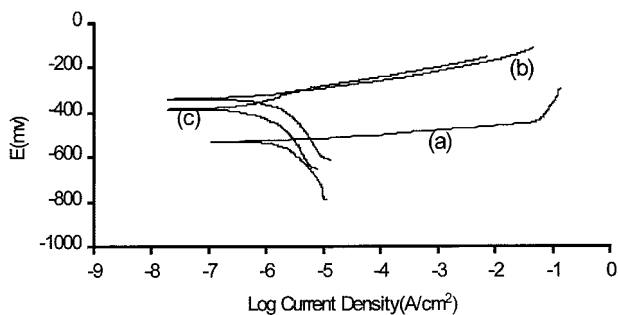
## RESULTS AND DISCUSSION

### Analysis of $E-t$ Curves

Figure 1 shows the typical  $E-t$  curves for aniline deposited onto Al-2024-T3. As shown in Figure 1, with an increase in the current density the electrode potential increases. To form a coating on aluminum galvanostatically, a minimum steady-state potential of 3.0 V versus SCE was required. This was also confirmed by cyclic voltametry,



**Figure 2** Tafel plots in 3.5 wt % of NaCl. (a) Bare Al-2024; (b) polyaniline-coated Al-2024 at 6 mA/cm<sup>2</sup> for 10 min.



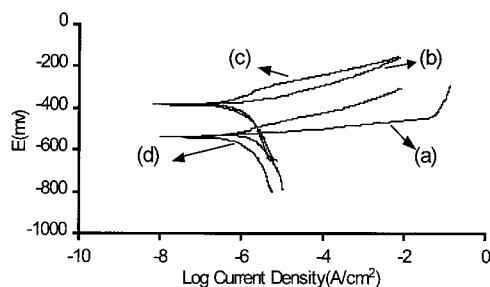
**Figure 3** Polyaniline coated on Al-2024 at 4 mA/cm<sup>2</sup> for different reaction times. (a) Control; (b) 5 min; (c) 10 min.

which showed no coating when the scan range was between  $-1.0$  and  $2.5$  V versus SCE.

### Analysis of Dc Polarization Studies

Figures 2–6 show the results obtained by dc polarization studies on Al-2024-T3. Figure 2 shows the comparison of Tafel plots of galvanostatically coated polyaniline at 6 mA/cm<sup>2</sup> for 10 min and the control (bare Al-2024). Figure 3 shows a Tafel plot of galvanostatically coated polyaniline at 4 mA/cm<sup>2</sup> for different reaction times along with the control. Figure 4 shows a Tafel plot of galvanostatically coated polyaniline on Al-2024-T3 at 2, 4, and 6 mA/cm<sup>2</sup> for 10 min.

As seen in Figure 2, both the control and the coated samples show similar cathodic behavior but significantly differ in the anodic behavior. It is shown that the anodic slope ( $\beta_a$ ) changes from  $18.49 \times 10^{-3}$  V/decade for the control to  $52.27 \times 10^{-3}$  V/decade for the aniline-coated sample. This shows that the coating acts as a barrier. There is a significant reduction in corrosion current and corrosion rate by polyaniline coating (Table I). The  $I_{\text{corr}}$  decreases from 1.703  $\mu\text{A}$  for the



**Figure 4** Polyaniline coated on Al-2024 at different current densities. (a) Control; (b) 2 mA/cm<sup>2</sup>; (c) 4 mA/cm<sup>2</sup>; (d) 6 mA/cm<sup>2</sup>.

**Table I** Comparison of  $I_{\text{corr}}$  and Corrosion Rate for Coated and Uncoated Al-2024

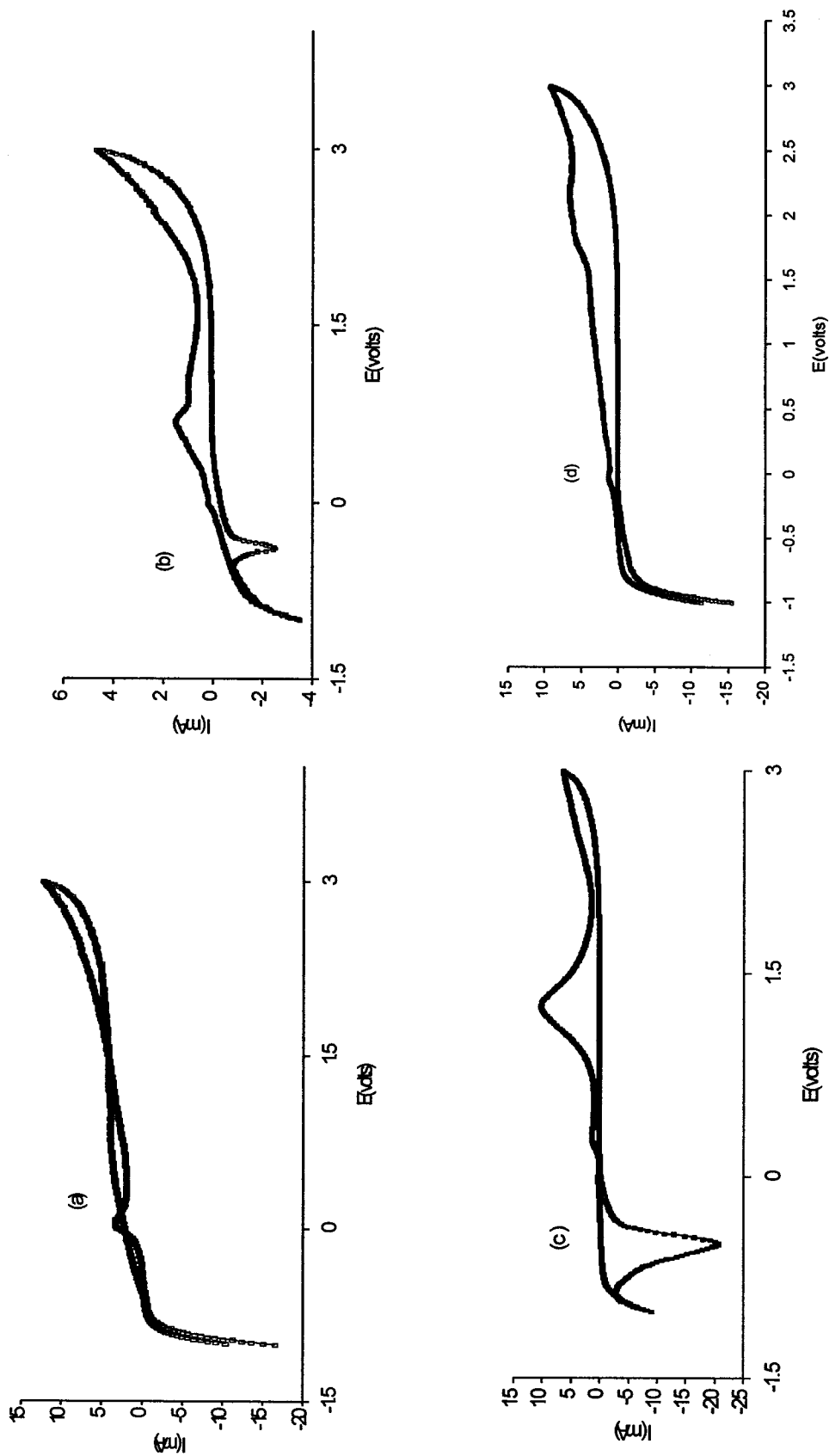
	Corrosion Rate (mmpy)	Corrosion Current ( $\mu\text{A}$ )
Control (bare Al-2024)	$2.3 \times 10^{-2}$	1.703
Polyaniline-coated Al-2024 (at 6 mA/cm <sup>2</sup> )	$7.4 \times 10^{-3}$	$5.43 \times 10^{-1}$

control to 0.543  $\mu\text{A}$  for the polyaniline-coated sample. The corrosion rate was decreased from 0.023 mmpy for the control to 0.0074 mmpy for the polyaniline coated aluminum (Table I). The corrosion rate for the coated sample is nearly threefold lower than that of the control.

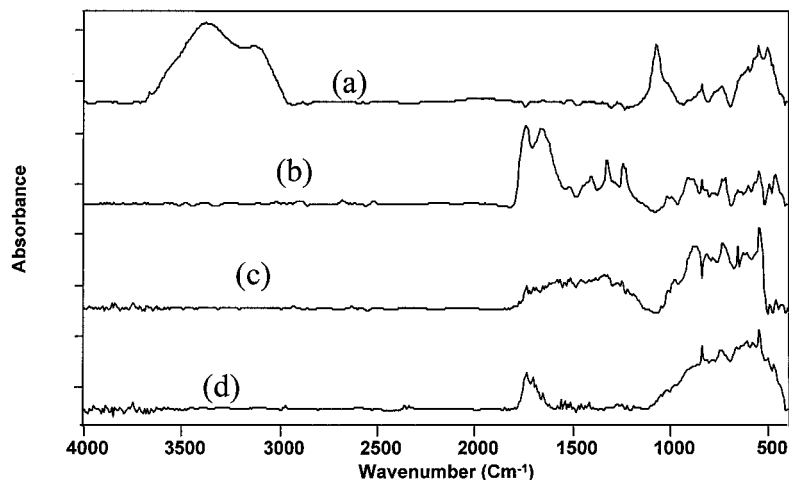
As shown in Figures 3 and 4 the  $I_{\text{corr}}$ , corrosion rate, and the corrosion potential are dependent on the reaction time and current density at which the sample is coated. The corrosion current is 1.53, 0.895, and 0.543  $\mu\text{A}$  for 2, 4, and 6 mA/cm<sup>2</sup>, respectively. Note that  $I_{\text{corr}}$  reduced by about one order of magnitude. We believe that as the current density increases, a more dense film with good barrier properties is formed onto the substrate. The  $E_{\text{corr}}$  for the coated samples is much higher than that of the control. Thus we can say that aluminum substrate approaches noble behavior.

### Cyclic Voltametry Studies

Figure 5 shows the cyclic voltametry results. As shown in Figure 5(a), we observe an anodic peak at 0.0 V versus SCE. We believe that this peak is attributable to the absorption and oxidation of hydrogen. Initially aluminum oxidizes to aluminum ions and the electrolyte oxalic acid dissociates into hydrogen and oxalate ions. The combination of the electron and the hydrogen ions gives rise to hydrogen gas, which adsorbs onto the substrate. When the reaction was carried out in the absence of any monomer (only oxalic acid), we observe the same peak as shown in Figure 5(d). As the number of cycles increases, the intensity of this peak decreases. This peak is no longer present in the fifth and the 25th cycle. With the increase in number of cycles we see another anodic peak at 1.0 V versus SCE and a corresponding cathodic peak  $-0.5$  V versus SCE. Because these are characteristic peaks for polyaniline, we can say that polyaniline is getting coated onto Al-2024-T3.



**Figure 5** Cyclic voltammograms for aniline (0.1M) in oxalic acid (0.3M) solution, (a) first cycle; (b) fifth cycle; and (c) 25th cycle; and oxalic acid (0.3M) solution, (d) first cycle.



**Figure 6** (a) Al-oxide and -hydroxide; (b) Al-oxalate; (c) aniline (0.3M) in oxalic acid (0.1M) solution, first cycle; (d) oxalic acid (0.3M) solution, first cycle.

### Infrared Spectroscopy (IR)

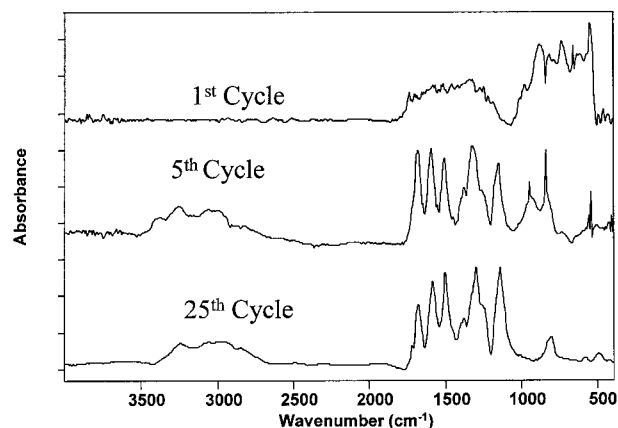
To understand the structure and composition of the polymer formed on the substrate, electropolymerization was stopped after various cycles during cyclic voltammetry and the IR spectra were taken. Figure 6 shows the IR spectra of Al-oxalate, Al-oxide, and hydroxide, the substrate after the first CV cycle [electrolyte-aqueous solution of aniline (0.1M) and oxalic acid (0.3M)] and the first cycle [electrolyte-aqueous solution of oxalic acid (0.3M)]. The spectra for the sample from CV's first cycle resemble the Al-oxalate spectra and are different from the Al-oxide and hydroxide spectra. The peak at  $1730\text{ cm}^{-1}$  can be assigned to the carboxylic group from oxalic acid. This peak can be seen in Figure 6b–d. Thus we believe that before the deposition of polyaniline, a passive layer of aluminum oxalate is formed on the substrate. Figure 7 shows the IR spectra for the samples of CV's first, fifth, and 25th cycles, respectively [electrolyte-aqueous solution of aniline (0.1M) and oxalic acid (0.3M)], respectively. The peaks at 1380, 1300, and  $1250\text{ cm}^{-1}$  are attributed to C–N stretching vibrations of aromatic amines. The peaks at 830 and  $1165\text{ cm}^{-1}$  are attributed to bending modes of C–H bonds. We also see peaks at 1500 and  $1590\text{ cm}^{-1}$ , which are attributed to the elongation vibration of the C–C bond of benzenoid and quinoid, respectively.<sup>17</sup> These peaks can be attributed to the formation of polyaniline on the substrate. We noted that as the number of cycles increases the intensity and sharpness of the peaks increase.

After comparing the IR spectra with the CV results, it can be inferred that the passivation of

aluminum initially occurred as a result of the deposition of the Al-oxalate layer on the surface; as the reaction proceeds polyaniline coating covers the passive layer. It is also suggested that the anodic peak at 1.0 V versus SCE and a cathodic peak at  $-0.5\text{ V}$  versus SCE are attributed to the formation of polyaniline onto the substrate.

### CONCLUSIONS

Polyaniline was successfully electrodeposited onto Al-2024-T3. The minimum potential required to form this coating was 3.0 V versus SCE. The dc polarization measurements showed that by coating polyaniline galvanostatically at  $6\text{ mA/cm}^2$  for 10 min, the corrosion rate was reduced



**Figure 7** Reflection absorption infrared spectra of polyaniline, deposited by CV onto Al-2024.

threefold compared to that of the control. It was shown that the  $I_{\text{corr}}$ , corrosion rate, and the corrosion potential were dependent on the current density and the reaction time for which polyaniline was coated onto the substrate. From the cyclic voltametry and the IR spectra we can infer that in the early stages of depositing of polyaniline, the passivation of the Al-2024-T3 surface occurred as a result of the deposition of an Al-oxalate layer on the surface. As the reaction proceeds the passive Al-oxalate film is subsequently covered by the polyaniline coating.

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