Corrosion behavior of PANI coated aluminum in oxalic acid containing different anions

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Abstract

Cyclic voltammetric studies were carried out on the deposition of polyaniline on pure aluminum from oxalic acid solution with and without different anions (CO_3^{-2}, SO_3^{-2}, SO_4^{-2}, DBS⁻) and contribution of these anions to lyaniline film formation was investigated. Corrosion behavior of polyaniline coated aluminum in oxalic acid solution with and without different anions (CO_3^{-2}, SO_3^{-2}, SO_4^{-2}, DBS⁻) has been investigated in 0.1 M HCl solution by polarization method. Semi logarithmic current-potential curves were obtained from which corrosion current density (i_{corr}), corrosion potential (E_{corr}), polarization resistance (R_p) and Tafel constants were determined. Polyaniline coating which was obtained in dodecylbenzenesulfonate (DBS⁻) containing oxalic acid was more effective than coatings obtained from other aninos in decreasing the corrosion rate.

Keywords: Electropolymerization; Aluminium; Anion; Corrosion

Introduction

In recent years, the interest towards the applications of conductive polymers in some fields such as biochemical capacitors [1], chargeable batteries [2] and corrosion protection [3–5] has increased. In a wide range of electrically conductive polymers, polypyrrole and polyaniline are the most promising conductive polymers which are used for protection against corrosion. Polypyrrole coating on aluminum surface has been fairly successful [6–8]. Nowadays, possibility of using polyaniline coatings as a new corrosion control technology has aroused interest [9–14].

It is known that polyaniline is a corrosion protective material for passivity of metals especially like iron and steel [15], aluminum and its alloys. Polyaniline is stable at high temperature, and easily synthesized. It has high conductivity with variable oxidation levels. Polyaniline can be chemically synthesized and can be coated on metal surface by electropolymerization of aniline from an appropriate environment which limits the substrate dissolve.

In the present were cyclic voltammetric studies on deposition of polyaniline on aluminum from different electrolyte media have bee made contribution of these anions to the polyaniline coating was also investigated.

Experimental

Voltammetric measurements made for the deposition of polyaniline films on aluminium (cyclic voltammetry) and polarization curves obtained for determining the corrosion

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rates of coated electrodes were performed using EG&G PAR Model 263 A Potentiostat-Galvanostat. 99.99 % pure aluminum electrode with a surface area of 0,785 cm² as working electrode, saturated calomel electrode (SCE) as reference electrode, Pt wire as counter electrode were used. The rest of the surface, which is out of the surface of the working electrode which is in touch with the solution, was coated by PTFE (polytetrafluoroethylene).

Before each experiment, working electrode was polished with emery paper (250,400,800 and 1200 mesh) and washed with twice distilled water. The electrode that had just passed this stage was immediately introduced in the electrochemical cell. All measurements were performed at room Temp. The concentrations of the solutions were fixed at 0.1 M.

The deposition of polyaniline films on aluminium was obtained between –1.0 V and +3.0 V (SCE) potential ranges at 50 mV/s scan rate after 30 cycles. All solutions were freshly prepared with twice distilled water. Polyaniline coated electrodes were washed with distilled water, after drying at room Temp. Current-potential curves were obtained at 10 mV/s scan rate.

Results and Discussion

Cyclic Voltammetry Studies and Effects of Different Anions

In order to determine the oxidation state of aniline, cyclic voltammogram of polyaniline formed on platinum electrode in 0.1 M $H_2C_2O_4$ was investigated. Cyclic voltammogram of aniline between –1.0 V and +3.0 V (SCE) potential ranges at 50 mV/s scan rate is given in Fig. 1.

Fig. 1. Cyclic voltammogram of platinum in 0,1 M $H_2C_2O_4$ + 0,1 M Aniline –1,0 V – 3,0 V (SCE) 50 mV/s

After deposition of polyaniline on platinum, green-coloured polyaniline film was observed. Oxidation potential of aniline was obtained approximately +0. 6 V (SCE) as seen from Figure 1. In order to prepare the polyaniline film on aluminum by adding 0.1 M aniline monomer into 0.1 M oxalic acid solution was added and a cyclic scan was performed between –1.0 V and +3.0 V (SCE) potential ranges at 50 mV/s scan rate. A transparent, sticky polyaniline film formation was observed. Cyclic voltammogram related to the polyaniline film growth is given as Fig. 2.
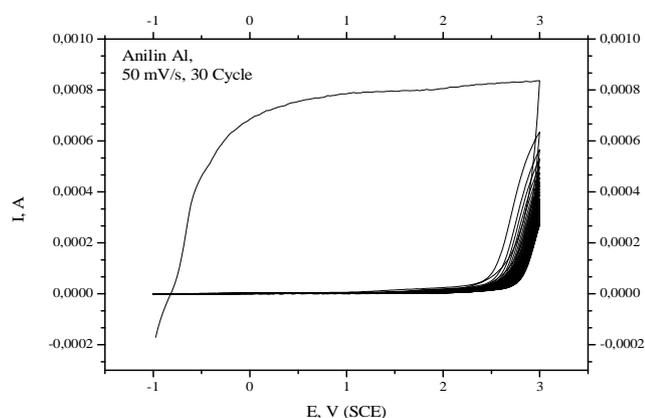

Fig. 2. Cyclic voltammogram of aluminum in 0,1 M $H_2C_2O_4$ + 0,1 M Aniline 50 mV/s

Oxidation peak (Fig. 1) seen at about +0.6 V on platinum electrode surface was not seen on aluminum electrode. Oxidation peak has completely disappeared (Fig. 2.). This is because, the PANI electrosynthesized on aluminum is a bilayer-film composed by a barrier type Al_2O_3 and electronically conducting PANI film [16]. Thus, by preventing the electron transfer at low scanning rate, Al_2O_3 has prevented the formation of oxidation peak of Aniline which was supposed to be seen at the first cycle [PANI→ PANI$^+$ + e^{-1}. A broad wave has been obtained at the first cycle. During the forward scan, the current increased in magnitude with increasing anodic potential to reach a value of approximately 0.8 mA at 3.0V. The

current decreased in magnitude during the reverse scan. This decrease shows that aluminum surface was coated with PANI.

Furthermore, it has also been thought that aluminum oxalate which formed on aluminum surface was effective in decreasing current. There is much evidence in literature [17,18] to suggest that the oxalate interacts with solid surface [2 Al^{+3} + $C_2O_4^{2-}$ Al_2 $(C_2O_4)_3$].

Current values decreased with number of scan (Fig. 2). This decrease in the current had the value of 0.0 A at the end of the thirtieth (30th) scan. This suggests that a homogeneous, sticky, transparent, tight and stable polyaniline film had been formed. Besides, the thickness of homogenous and sticky PANI film increased with number of scan.

Contribution of anions to dopant effect of oxalic acid has been investigated. Cyclic voltammograms of electrochemically PANI coated Aluminum in 0,1 M Aniline + 0,1 M oxalic acid +0.1 M different anions (CO_3^{-2}, SO_3^{-2}, SO_4^{-2}, DBS$^-$) have been given as Fig. 3,4,5 and 6 respectively.

Cyclic voltammogram which was obtained for to the oxalate/carbonate/PANI system is given in Figure 3. A wide peak was obtained in the first cycle, and in the forward scan current showed an increase with a decrease in the reverse scan. Especially in the second scan, a significant decrease was seen (Fig. 3). Current decreased as the number of scans increased. This decrease was about 75 % at the end of the 30th scan. $Al_2(CO_3)_3$ layers that was expected to be formed on the surface is thought to be effective on the current decrease as well as the polyaniline film which was formed on aluminum surface with oxalate/carbonate/PANI system. Cyclic voltammogram curves that were obtained with PANI coating deposited on aluminum in oxalic acid containing SO_3^{-2}, SO_4^{-2}, DBS$^-$ anions (Figures 4 to 6) show similarity to the curve that was obtained for to oxalate-PANI system (Figure 2).

At the first cycle, a wide peak was obtained in each of the curves (Figures 3 to 6). Current increased in the forward scan, while the current decreased in the reverse scan, and reached the value of 0.0 A. In all curves, current value decreased with increasing number of scans. Thus, hard and homogenous PANI film layer was formed on aluminum surface. Similarities of cyclic voltammograms that were obtained for oxalate / PANI and oxalate /anion / PANI suggest that anions did not contribution much to dopant effect of oxalate. It is thought that when oxalic acid solution containing different anions was used as a dopant, along with oxalate, other anions also interact with positively charged polymer chain. Interaction between bivalent ions such as CO_3^{-2}, SO_3^{-2}, SO_4^{-2} and monovalent ions like DBS$^-$ has been shown schematically below.
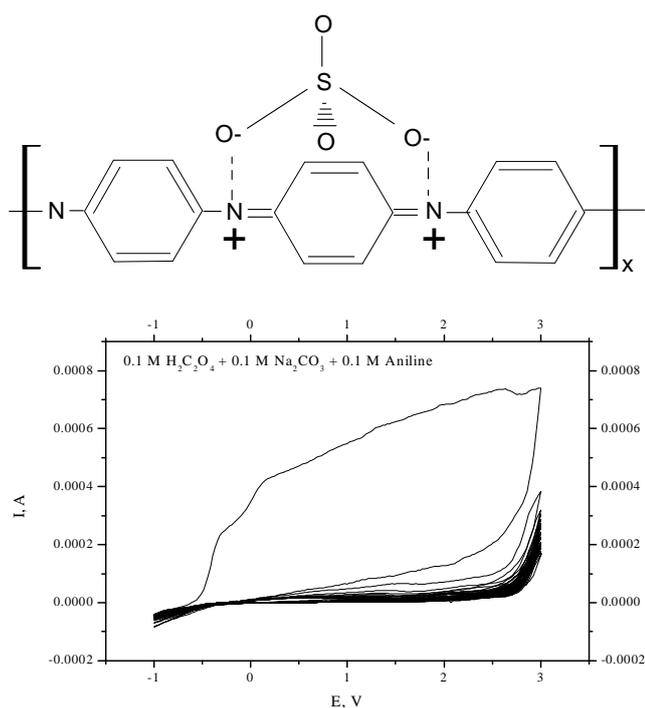
Fig. 3. Cyclic voltammogram of aluminum in 0.1 M $H_2C_2O_4$ + 0.1 M Na_2CO_3 +0.1 M Aniline. 50 mV/s ,30 cycle.
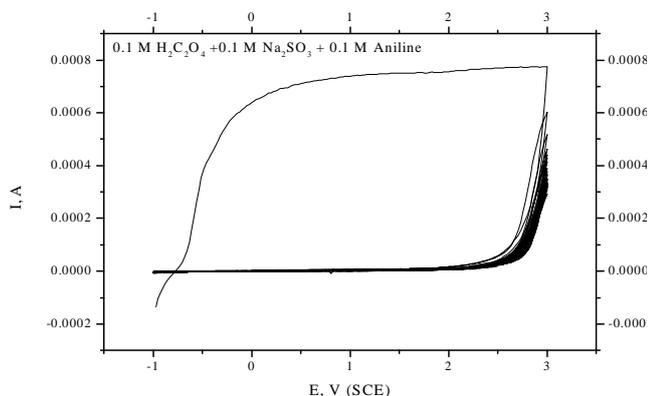

Fig. 4. Cyclic voltammogram of aluminum in 0.1 M $H_2C_2O_4$ + 0.1 M Na_2SO_3 +0.1 M Aniline . 50 mV/s ,30 cycle.
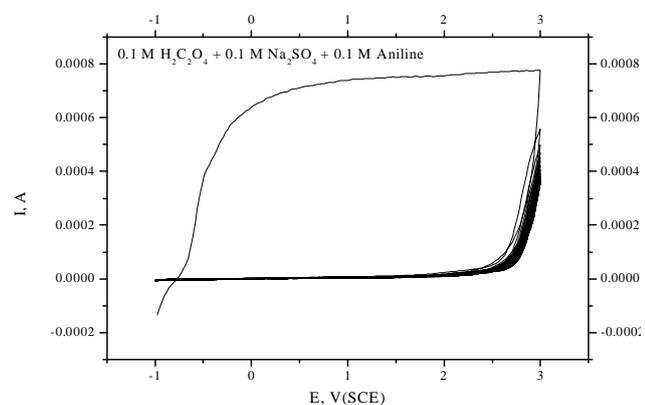

Fig. 5. Cyclic voltammogram of aluminum in 0.1 M $H_2C_2O_4$ + 0.1 M Na_2SO_4 +0.1 M Aniline .50 mV/s ,30 cycle.
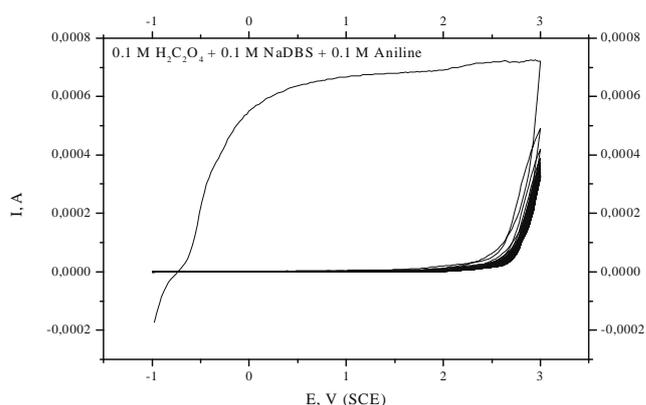

Fig. 6. Cyclic voltammogram of aluminum in 0.1 M $H_2C_2O_4$ + 0.1 M NaDBS +0.1 M Aniline . 50 mV/s ,30 cycle.

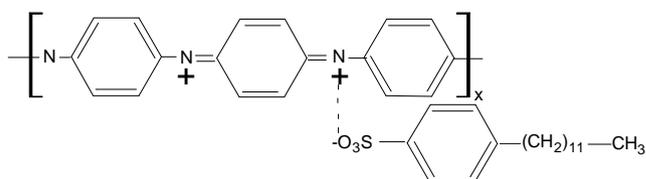The proposed chemical structure of PANI/SO_4^{-2} and PANI / DBS^- given in Fig. 7.

Fig. 7. The proposed chemical structure of PANI/SO_4^{-2} and PANI/DBS^-

Because of the release of H^+ during electropolymerization shift of the equilibrium: $[C_2O_4^{2-} + H^+ HC_2O_4^-]$ in the direction of bioxalate formation. In this situation, mono charged oxalate anion forms bipolaron layer which is more effective than di charged oxalate anion. Thus, the bulky arrangement of two monodeprotonated oxalic acid species would account for the shielding of bipolaron polyaniline chain from nucleophilic attack [16] (Fig. 8).
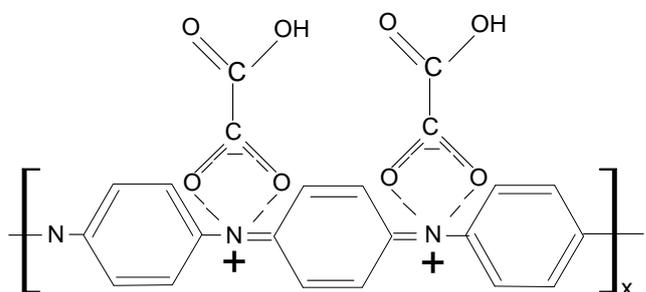

Fig. 8. Schematic representation of the shielding effect of oxalate anions from nucleophilic attack of bipolaron sites of polyaniline.

So, it appears that the oxalate dopant has a stabilizing effect on the polymer films, minimizing breakdown of polyaniline when cycled to high potential. In that case, the polymer is more stable when formed in oxalate solution despite the high potentials used in the electropolymerization process.

It is thought that ion radius, diffusion, adsorption and also, electrostatic force between positively charged polymer chain and molecules have been effective in PANI / ion interaction.

Corrosion Behavior

Corrosion behavior of PANI coated aluminum in oxalic acid solution with (CO_3^{-2}, SO_3^{-2}, SO_4^{-2}, DBS^-) and without different anions in 0.1 M HCl solution have been investigated. Polarization curves have been given in Figure 9. Corrosion current density (i_{corr}), corrosion potential (E_{corr}), polarization resistance (R_p) and coating efficiency values are the electrochemical parameters which were obtained in 0.1 M HCl solution of PANI coated aluminum by adding different anions (CO_3^{-2}, SO_3^{-2}, SO_4^{-2}, DBS^-) into oxalic acid solution as shown in Table I.
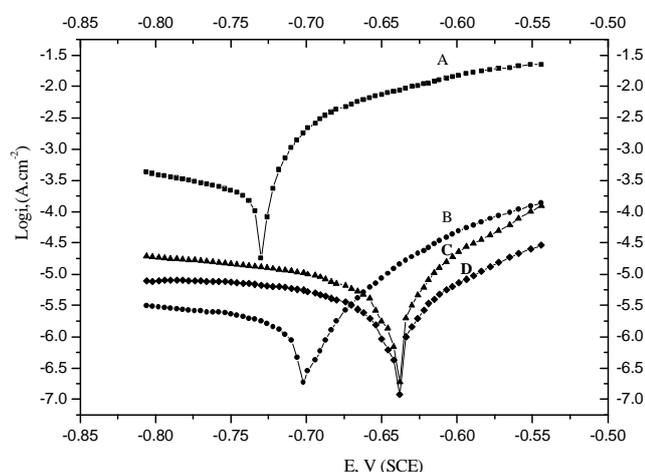

Fig. 9. Polarization curves of aluminium in 0.1 M HCl A:uncoated Al, B:Al/oxalate/CO_3^{-2}/PANI, **C**: Al/oxalate/SO_4^{-2}/PANI, **D**:Al/ oxalate/DBS^-/PANI.

Table I
Electrochemical parameters for coated and uncoated aluminum in 0.1 M HCl

	I_{corr} ($\mu A/cm^2$)	E_{corr} (mV)	R_p (ohm)	Efficiency of coating % (EC)
0.1 M HCl (for uncoated Al)	391.1	–754.8	18.9	–
Al/oxalate/PANI	6.0	–645.8	5616.9	98.5
Al/oxalate/CO_3^{-2}/PANI	2.8	–722.0	8534.8	99.3
Al/oxalate/SO_3^{-2}/PANI	7.1	–644.1	4651.7	98.2
Al/oxalate/SO_4^{-2}/PANI	5.4	–640.7	5830.1	98.6
Al/oxalate/DBS^-/PANI	2.3	–635.7	12158.1	99.4

$$\text{Efficiency of coating(EC)} = \frac{(I_{corr})\text{uncoated} - (I_{corr})\text{coated}}{(I_{corr})\text{uncoated}} \times 100$$

In 0.1 M HCl, PANI coated aluminum containing SO_3^{-2} and SO_4^{-2} anions in oxalic acid solution decreased the corrosion current density by 98.2% in oxalate / sulfite / PANI system and by 98.6 % in oxalate / sulfate /PANI system (Table I).

In addition, it has been found that the coating which was obtained using oxalate / carbonate / PANI system decreased the aluminium corrosion rate by 99.3 %. The polyaniline coating made in oxalic acid in the presence of CO_3^{-2} anion was more adherent and homogeneous than in the presence of SO_3^{-2} and SO_4^{-2}.

In oxalate /carbonate / PANI film, in addition to the polymer that formed on the surface, $Al(OH)CO_3$ was effective.

The coating that was obtained in 0.1 M HCl solution using oxalate /DBS^- /PANI system has decreased the corrosion rate by 99.4% (Table I). In this decrease, besides the aluminum oxalate passive layer which is formed on aluminum surface, $PANI^+DBS^-$ layer (which is formed by the combination of $PANI^+$ and DBS^- on the metal surface) is thought to be effective. Thus more homogeneous, tight and stable polyaniline coating was obtained on the aluminum surface. DBS^- showed surface active properties. So micellar media affected the electrochemical reactions by irreversible adsorptions, leading to a change in the solution-electrode interface properties.

Corrosion prevention effect of PANI coated aluminum which was obtained in oxalic acid solution containing SO_3^{-2}, SO_4^{-2} anions and prevention effect of oxalate /PANI film changed. PANI film layer which was formed in oxalate / PANI and oxalate / anion /PANI system blocked the transfer of active Cl^- ions to the metal –solution interface, and the corrosion rate was decreased.

Conclusions

A homogenous, stable, hard PANI film layer was formed electrochemically on aluminum surface from oxalic acid solution with and without different anions.

Added anions did not have much contribution to dopant effect of oxalic acid in electrochemically PANI coating of aluminum surface.

PANI coatings decreased the corrosion rate of aluminum. Polyaniline coating obtained from dodecylbenzenesulfonate (DBS^-) containing oxalic acid was more effective than the other anions in decreasing the corrosion rate of aluminum in 0.1 M HCl.

Acknowledgment

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