

Electrodeposition of Polypyrrole on Aluminium in Oxalic Acid

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Summary: Adherent and homogenous polypyrrole films were electropolymerized onto aluminum from aqueous oxalic acid and oxalic acid containing different anions (SO_3^{2-} , SO_4^{2-} , CO_3^{2-} , DBS^-) by cyclic voltammetry. The corrosion behavior of coated and uncoated aluminum with polypyrrole was investigated in 0.1 M HCl by potentiodynamic polarization method. Inhibition effect of anions onto uncoated aluminum was determined in 0.1 M HCl. The curves of anodic and cathodic polarization were obtained. The electrochemical parameters were determined from the polarization curves. The efficiency of polypyrrole coating on aluminum was calculated. It was shown that thin PPy film had provided good corrosion protection of aluminum in 0.1 M HCl. Oxalate | DBS^- | PPy system had showed the most superior corrosion protection properties than other anion systems.

Introduction

Different methods are used in order to prevent metal corrosion. Because such features have made conductive polymers economically and safely available by electrochemical methods in the recent years, their forms oxidizing status of the conductive polymers are used in metal corrosion prevention of iron [1], steel [2, 3], zinc, aluminum and other oxidizable metals [1-5].

Delocalizing π -conjugated system through doping conductive polymers raises their conductivity much more as well [5]. Pyrrole is one of the most important materials in conductive polymers. The lower oxidation pyrrole (Py) compared to commonly used monomers enables the possibility of obtaining PPy films on active metals. PPy has been electropolymerized into a variety of substrates with promising anticorrosion properties [5-10].

Doping pyrrole with different organic and inorganic ions enables the forming of polymers and deposit polymers on substrate. The nature of working electrode also plays as an important role in polypyrrole synthesis as the nature of dopant ion. The working electrode should be oxidized with monomer at the same time. The protective, uniform and thin film layer correspondingly formed on the surface of aluminum impedes the process of electropolymerization.

In this study, electropolymerization of polypyrrole on aluminum was researched in two sections. In the first Section: the corrosion behavior

of the uncoated and aluminum coated with polypyrrole in oxalic acid was researched in the hydrochloric acid containing and not containing different anion by the method of potential dynamic polarization. In the second section: the corrosion behaviors of uncoated and coated aluminum obtained by depositing polypyrrole in oxalic acid containing different anion was researched in 0.1 M HCl.

Results and Discussion

Cyclic Voltammetry

Polypyrrole coatings are electrochemically deposited on aluminum in oxalic acid by cyclic voltammetry. Fig. 1. show the cyclic voltammogram obtained in oxalic acid at the scan rate of 50 mV/ s. The first cycle shows an oxidation pick (in Fig. 1). As seen from the figure, an anodic peak approximately of 0.0 V is observed [5, 6, 10].

In the formation of the first cycle;

- I. Initially, aluminum ions are formed by oxidation of aluminum (eq. 1).
- II. Oxalic acid is dissociated to oxalate ions and positive hydrogen ions (eq. 2).
- III. These positive hydrogen ions that the electrons have lost by the oxidation of aluminum are combined to give hydrogen gas (eq. 3).
- IV. The hydrogen gas, thus obtained adsorbs onto the working electrode and oxidized to positive hydrogen ions (eq. 4). It is determined in the

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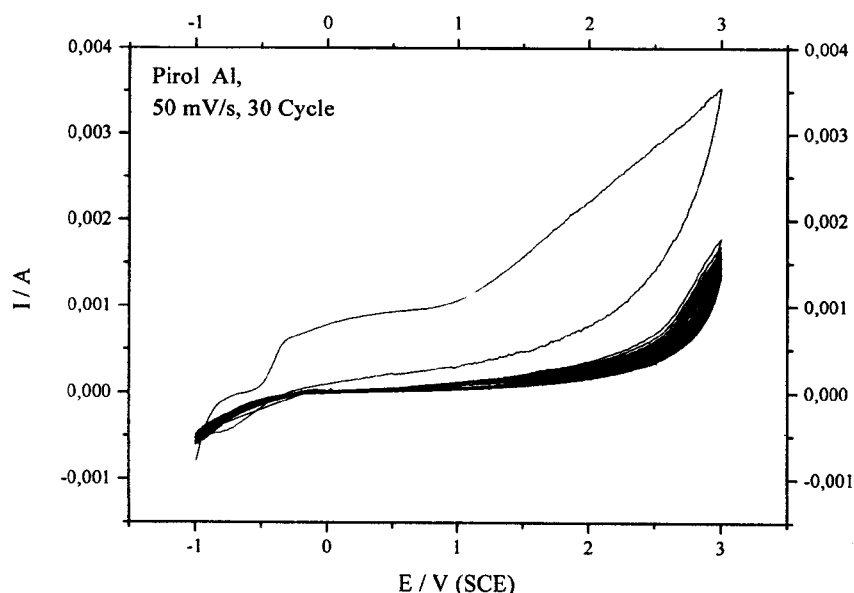
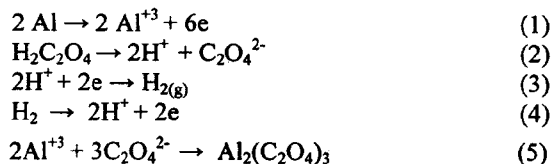


Fig. 1: Cyclic voltammograms of PPy-coated Al electrode in 0.1 M oxalic acid at 50 mV.s⁻¹

previous studies that hydrogen is adsorbed at this point [5, 14].



During the forward scan, the current increases in magnitude with increasing anodic potential to reach a value of approximately 3 mA at 3.0 V (SCE). The current decreases in magnitude during the reverse scan. This is consistent with the formation of an anodized layer on aluminum electrode. Oxidation peak is observed only in the first cycle. This peak is related to the oxidation of the monomer [PPy \rightarrow PPy⁺ + e]. The current is decreased with increasing number of scans. This can be explained by combining together of aluminum ions with oxalate ions to form passive layer of amorphous aluminum oxalate (eq. 5) [5]. Adherent, homogenous, black and thick polypyrrole films are electropolymerized onto aluminum in oxalic acid. This adherence could be due to absence of strong binding between metal and polymer.

There is no noticeable corresponding cathodic peak in the reverse scan implying that the

reaction becomes completely irreversible. Cathodic peak was not seen due to the fact that polypyrrole film formed on the surface prevented the formation of hydrogen.

The cyclic voltammograms of aluminum in oxalic acid solution containing different anions (CO₃²⁻, SO₃²⁻, SO₄²⁻, DBS⁻) are given in Figs. 2-5. The anodic oxidation peak obtained in the first cycle in the oxalate | PPy system has completely faded out in the first cycle in the oxalate | sulfide | PPy and oxalate | carbonate | PPy systems and a large wave is obtained. The cathodic peak due to formation of Al₂(CO₃)₃ and Al₂(C₂O₄)₃ layers in the Oxalate | Carbonate | PPy system and Al₂(SO₃)₃ and Al₂(C₂O₄)₃ layers on aluminum surface in the Oxalate | Sulfide | PPy system are not seen (Fig. 2, 3). During the back sweep, the current density decreases considerably and reaches a very weak value, which remains nearly constant during the second anodic and cathodic sweep, this indicates an important passivation of aluminum surface.

The cyclic voltammogram curve obtained with PPy coating deposited on aluminum in oxalic acid containing SO₄²⁻ anion (Fig. 4) looks like that obtained from the Oxalate | PPy system (Fig. 1). This shows that the SO₄²⁻ anion does not contribute the dopant effect of oxalic acid.

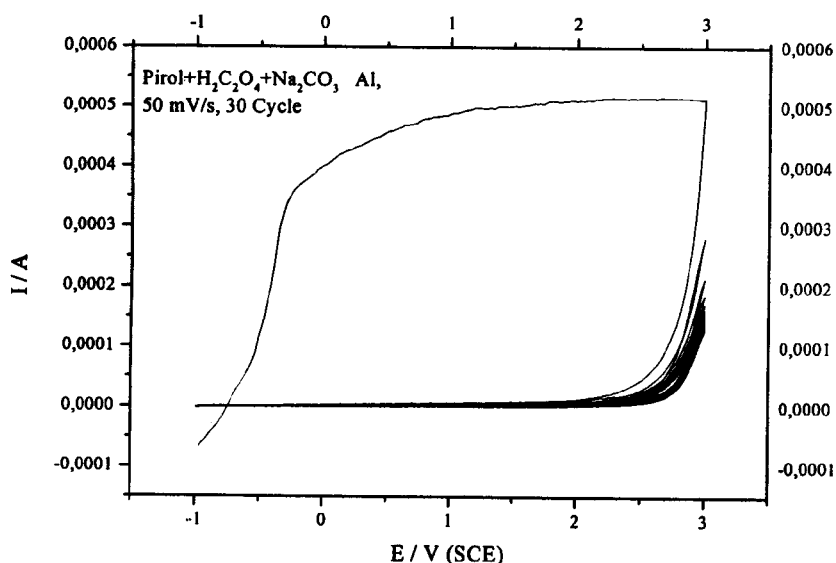


Fig. 2: Cyclic voltammograms of PPy-coated Al electrode in 0.1 M oxalic acid containing 0.1 M Na_2CO_3 at $50 \text{ mV}\cdot\text{s}^{-1}$

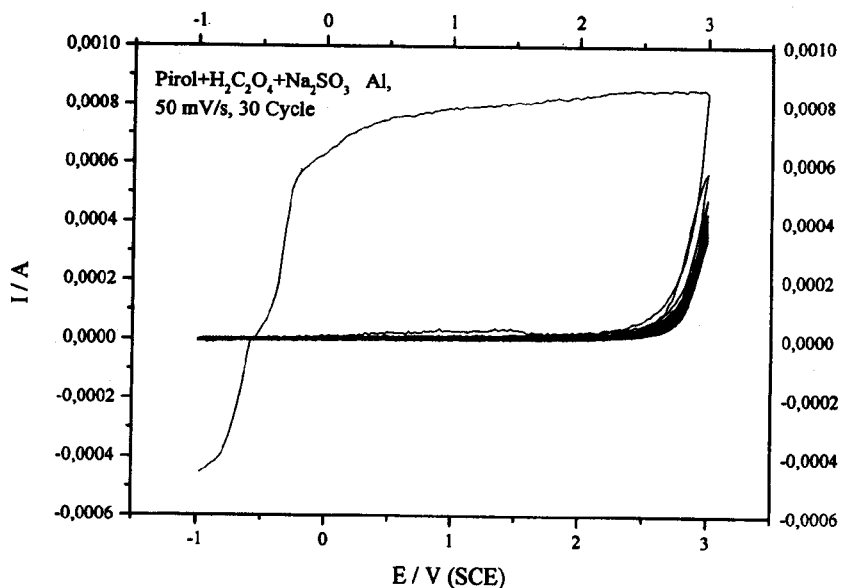
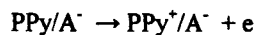


Fig. 3: Cyclic voltammograms of PPy-coated Al electrode in 0.1 M oxalic acid containing 0.1 M Na_2S at $50 \text{ mV}\cdot\text{s}^{-1}$

The cyclic voltammogram of Oxalate $|\text{DBS}^-|$ PPy system is seen in Fig. 5. The peak potential in the first cycle is shifted to higher positive value. It is thought that being adsorbed on the aluminum surface of DBS^- anions decreases the rate of electron transfer. In this case the anodic current peak corresponds to the reaction:



There is no corresponding cathodic peak in the reverse scan implying that this process is irreversible. With the increasing number of scans a sharp decrease in the current value has been observed (Fig. 5). Anionic surfactants, such as SDBS, form micelles (in solution) and bilayered micelles (on

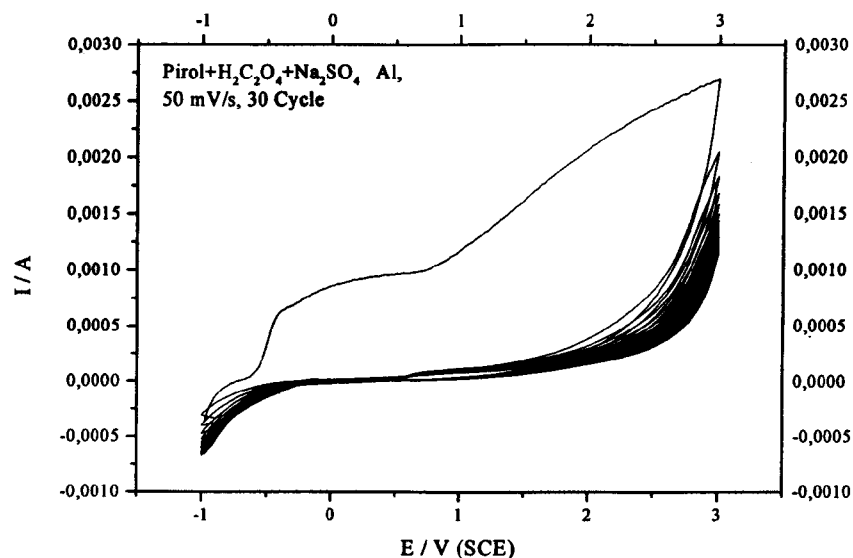


Fig. 4: Cyclic voltammograms of PPy-coated Al electrode in 0.1 M oxalic acid containing 0.1 M Na_2SO_4 at $50 \text{ mV}\cdot\text{s}^{-1}$

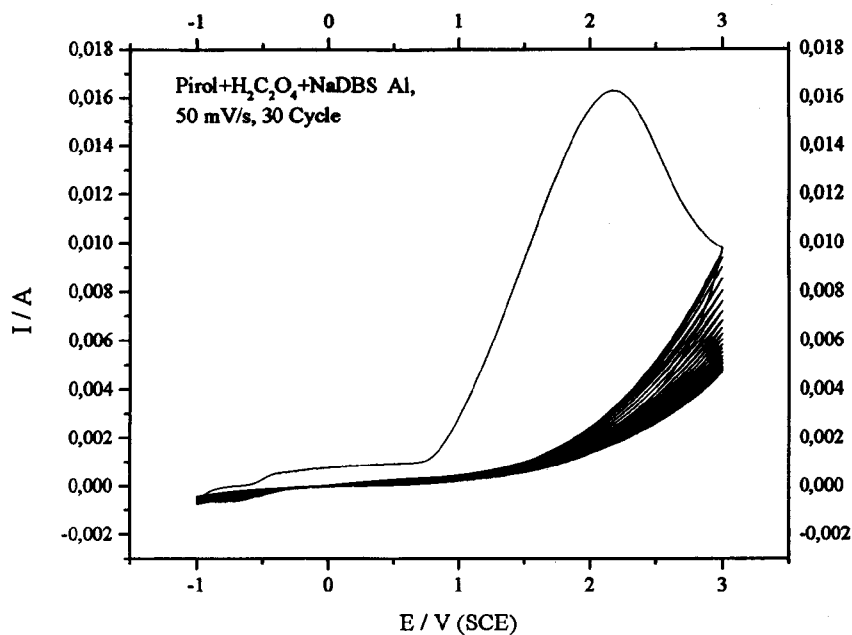


Fig. 5: Cyclic voltammograms of PPy-coated Al electrode in 0.1 M oxalic acid containing 0.1 M NaD at $50 \text{ mV}\cdot\text{s}^{-1}$

electrode surfaces) in aqueous solutions. So, it is thought that rectangular micelles form easily on aluminum electrodes because of the influence of hydrophilic oxide layers on the electrode surface. The thickness of uniform, adherent, homogenous PPy films are obtained regularly with increasing number of cycles. The experimental results are shown that the

best pyrrole coating is obtained in the oxalic acid solution containing DBS^- anion.

Corrosion Behavior

Some of the polarization curves in the 0.1 M HCl with and without different anions (NO_2^- , CO_3^{2-} ,

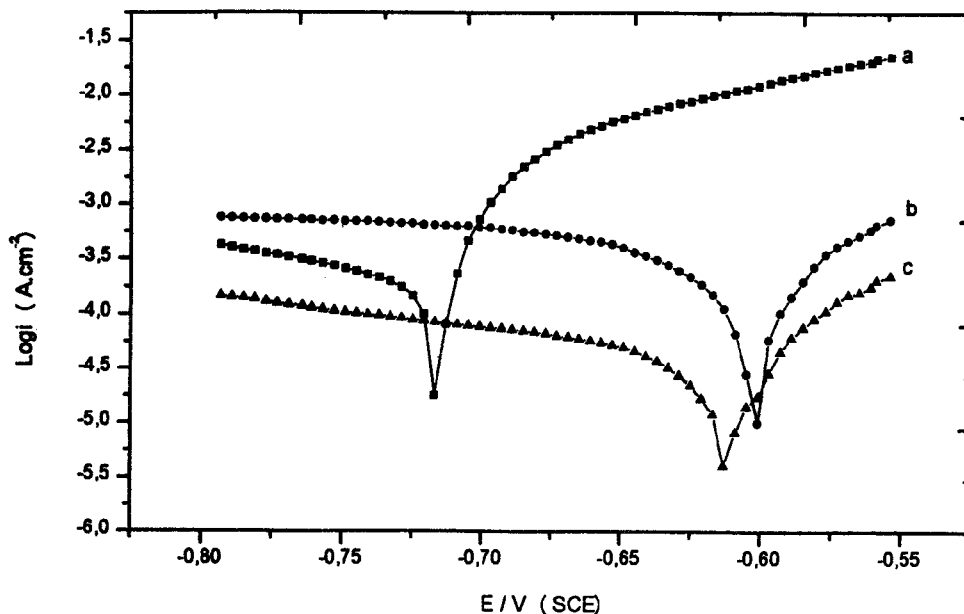


Fig. 6: Polarization curves for a : uncoated aluminium electrode in 0.1 M HCl b : uncoated aluminium electrode in 0.1 M HCl containing 0.1M Na₂SO₃ c: PPy-coated aluminium electrode in 0.1 M HCl.

Table-1: The Electrochemical parameters of uncoated aluminium obtained in 0.1 M HCl with and without different anions.

Conc.	<i>I</i> _{corr} (μA)	<i>E</i> _{corr} (mV)	<i>R</i> _p	<i>E</i> %
0.1 M HCl	391.1	-754.8	18.9	
0.1 M HCl + 0.1 M NaNO ₂	359.4	-579.5	82.5	8.2
0.1 M HCl + 0.1 M Na ₂ CO ₃	11.8	-629.8	2421.1	96.9
0.1 M HCl + 0.1 M Na ₂ SO ₃	258.9	-599.0	168.8	33.8
0.1 M HCl + 0.1 M Na ₂ SO ₄	12.2	-757.9	1196.1	96.8
0.1 M HCl + 0.1 M Na ₂ CrO ₄	0.6	-608.8	24245.6	99.8
0.1 M HCl + 0.1 M NaDBS	11.6	-669.1	2531.9	97.03

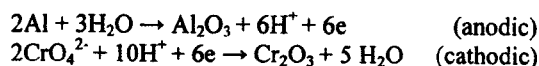
SO₃²⁻, SO₄²⁻, DBS⁻) of aluminum uncoated and coated with PPy in oxalic acid are shown in Fig. 6. The electrochemical parameters of the uncoated aluminum in 0.1 M HCl with and without different anions are given in Table-1. The inhibition efficiency of different anions on uncoated aluminum is calculated as follows;

$$\text{Efficiency of inhibition} = \frac{(I_{\text{corr}})_0 - (I_{\text{corr}})_1}{(I_{\text{corr}})_0} \times 100$$

(*I*_{corr})₀ corrosion current density without inhibitor,
(*I*_{corr})₁ corrosion current density with inhibitor

The current density of uncoated aluminum in HCl solution containing CrO₄²⁻ anion is decreased and exhibited the inhibition efficiency the rate of 99.8

%. The inhibition effect of chromate anions may be due to the reduction of Cr⁺⁶ in the chromate to Cr⁺³ (as Cr₂O₃) during film formation according to [15]:



Thus, the corrosion rate of aluminum is controlled by the partial cathodic reaction

The inhibition efficiency of DBS has been determined as % 97.03. (Table-1). Because of being adsorbed on the electrode surface, DBS⁻ anion is blocking the surface and hindering metal corrosion [12, 13].

The corrosion rate of aluminum uncoated in HCl solutions containing CO₃²⁻ and SO₄²⁻ anions has also significantly decreased. Besides the Al₂O₃ layer formed on the aluminum surface, the formation of passive Al₂(CO₃)₃ and Al₂(SO₄)₃ has become effective.

It has been observed that NO₂⁻ and SO₃²⁻ anions are not effective to the corrosion rate of uncoated aluminum in HCl solutions as CrO₄²⁻, DBS⁻, CO₃²⁻ and SO₄²⁻. This has shown that NO₂⁻ and SO₃²⁻ anions could not form a uniform and protective film layer on the electrode surface.

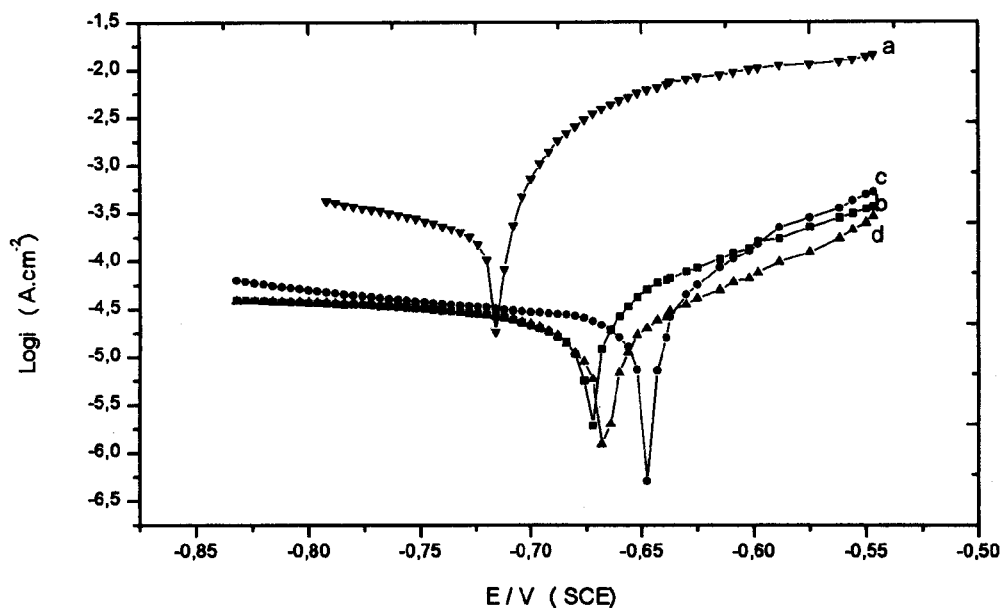


Fig. 7: Polarization curves of aluminum in 0.1 M HCl a: uncoated aluminium electrode b: PPy-coated Al in oxalic acid containing 0.1 M Na_2CO_3 c: PPy-coated Al in oxalic acid containing 0.1 M Na_2SO_4 d: PPy-coated Al in oxalic acid containing 0.1 M Na_2SO_3 .

Table-2: The Electrochemical parameters of aluminum coated with PPy in oxalic acid with and without different anions (SO_3^{2-} , SO_4^{2-} , CO_3^{2-} , DBS) obtained in 0.1 M HCl.

Conc.	I_{corr} (μA)	E_{corr} (mV)	R_p	EC %
Oxalate / PPy	66.9	-614.3	819.1	82
Oxalate / SO_3^{2-} / PPy	23.6	-656.1	2662.4	94
Oxalate / SO_4^{2-} / PPy	17.6	-644.3	3160.2	95.5
Oxalate / CO_3^{2-} / PPy	20.4	-672.6	2967.7	94.8
Oxalate / DBS ⁻ / PPy	0.1	-527	222707.7	99.9

The percent efficiency of coating values was also calculated by using the following equation and is given in Table-2:

$$\text{EC \%} = \frac{(I_{\text{corr}})_{\text{uncoated}} - (I_{\text{corr}})_{\text{coated}}}{(I_{\text{corr}})_{\text{uncoated}}} \times 100$$

$(I_{\text{corr}})_{\text{uncoated}}$, corrosion current density of the uncoated metal, $(I_{\text{corr}})_{\text{coated}}$, corrosion current density of the coated metal

The polarization curves of aluminum coated with PPy in oxalic acid with and without different anions (SO_3^{2-} , SO_4^{2-} , CO_3^{2-} , DBS⁻) are obtained in 0.1 M HCl and given in Fig. 7. Fig. 7 a-d, which shows that corrosion rates of coated electrodes are lower than corrosion rate of uncoated electrode. The

coating efficiency of coated aluminum covered with PPy in oxalic acid has been determined as 82 % in 0.1 M HCl. When anion is added into oxalic acid, the aluminum coating efficiency within 0.1 M HCl has increased. And this shows that coating is much more rigid and protective in oxalic solution including anion. The most effective coating has been obtained in oxalate |DBS⁻| PPy system. The corrosion rate of the aluminum coated with PPy in oxalic acid containing anion is decreased according to the oxalate | PPy system. This decrease is at most in the oxalate |DBS⁻| PPy system and by the rate of 99.9 %. So more homogenous, rigid and adherent polypyrrole layer is deposited on the aluminum from a solution oxalic acid containing DBS⁻ anion.

The inhibition efficiency in the solution of 0.1 M HCl including CrO_4^{2-} has the same value as aluminum coating efficiency coated with oxalate |DBS⁻| PPy (comparison between Fig. 1 and 2). However CrO_4^{2-} anion is not preferred due to its toxic effect.

Experimental

Electrodes were prepared from high purity aluminum (99.99 %). The electrodes were provided in rod form. Suitable lengths of the rods were

embedded in epoxy resin in a Teflon holder to give a surface area of 0.785 cm². Electrical contact was achieved by means of a copper wire threaded into the base of the metal sample. Prior to each test, the exposed surfaces were polished to a smooth surface finish, using 1200 SiC and rinsed with acetone and distilled water and dried after and transferred to electrochemical cell. All chemicals were purchased from Aldrich Chemical Company and used without any further purification. All the solutions were prepared with distilled water. The measurements were taken at room temperature.

The electropolymerization was carried out in 0.1 mol.dm⁻³ pyrrole and 0.1 mol.dm⁻³ oxalic acid with and without different salts (0.1 M Na₂CO₃, 0.1 M Na₂SO₃, 0.1 M Na₂SO₄, 0.1 M NaDBS). The polypyrrole films were grown on aluminium in a conventional three electrode cell for a period of 30 min. at room temperature and in aqueous solutions which were previously stirred.

The electrochemical measurements were carried out using an EG &G Potentiostat Model 263 A. Platinum wire counter electrode and Saturated Calomel Electrode (SCE) were used in conventional three compartment as reference electrode and aluminum electrode as working electrode. All the potentials were measured against the saturated calomel electrode (SCE). Cyclic voltammetry was used as the deposition technique. CVs were recorded uniformly at a scan rate of 50 mV/s by sweeping the potential between -1.0 and +3.0 V against SCE. The deposition was carried out in 30 continuous scans. The corrosion behavior of coated and uncoated aluminum was carried out in 0.1 M HCl by potentiodynamic method. At the same time, inhibition effect on aluminum corrosion of different salts as NaNO₂, Na₂CO₃, Na₂SO₃, Na₂SO₄, Na₂CrO₄, NaDBS were determined using by potentiodynamic polarization.

Conclusion

Adherent and homogenous polypyrrole films were obtained onto aluminum in oxalic acid. It was determined that the aluminum coated in oxalate | PPy was effective in decreasing the corrosion rate in 0.1 M HCl.

Homogenous and more rigid polypyrrole coatings on the aluminum surface were obtained with the addition of different anions in oxalic acid. The coating obtained from the oxalate | anion | PPy system has been effective in decreasing the corrosion rate of aluminum in 0.1 M HCl. It was found that the coating formed with cyclic voltammetry to the oxalate | DBS⁻ | PPy system was especially more rigid and homogenous and this was also more effective in decreasing the corrosion rate of aluminum.

Acknowledgments

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