



Effect of doping by corrosion inhibitors on the morphological properties and the performance against corrosion of polypyrrole electrodeposited on AA6061-T6

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ABSTRACT

This paper describes the electrosynthesis of polypyrrole (PPy) onto AA6061-T6 aluminum alloy from a sulfuric acid solution doped with molybdate anions (MoO₄²⁻) or 8-hydroxyquinoline (8HQ) species. These dopant compounds were chosen as they have been proven to be effective in mitigating the corrosion in chloride medium. The protectiveness of PPy coatings incorporating these corrosion inhibitors within the polymer matrix is discussed. The coatings were morphologically characterized via scanning electron microscopy (SEM) and evaluated electrochemically via polarization in 0.5 M NaCl. The results show that doping PPy with molybdates or 8HQ changes its morphological properties and its effectiveness in preventing passivity loss for AA6061-T6 in chloride media.

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1. Introduction

The prevention or minimization of aluminum oxidation is a major problem in the automotive and aerospace industries. The technique usually adopted to protect Al alloys concentrates on the barrier concept through the application of a conversion coating obtained by phosphate and chromate based pretreatments. However, the undesirable impacts of such conversion processes on the environment have driven manufacturers to search for alternative processes [1].

It is in this perspective that the conjugated polymers are considered as an environmentally promising alternative against corrosion of metallic materials [2,3]. Polypyrrole (PPy) is currently considered as one of the best organic materials which can significantly reduce corrosion of aluminum [4–6].

The electrochemical polymer synthesis on metallic surface keeps attracting the attention of researchers for the electroelaborated polymer quality. This polymerization method offers a

large overview and flexibility of polymer properties since they are highly influenced and modulated by synthesis medium and conditions [7,8].

By a judicious choice of the supporting electrolyte, it is possible to improve the efficiency of the electrodeposition of polypyrrole.

Recently it was shown that the electrochemical synthesis of conducting polymers in a medium enriched by inhibitors species reduced the metal degradation [9].

A wide variety of organic and inorganic compounds have been demonstrated as effective inhibitors against corrosion, among which the molybdate anions (MoO₄²⁻) and 8-hydroxyquinoline (8HQ) (Fig. 1).

Breslin et al. [10] suggested that molybdates intervene via their oxidizing power in the growth of the passive layer. Bazzi et al. [11] have established that molybdate ions act on the anodic process by minimizing the sensitivity of aluminum and its alloy to pitting corrosion.

Some research has found that 8-hydroxyquinoline protects aluminum against pitting corrosion by forming an insoluble chelate layer [12]. According to Gaarrigues et al. [13], 8HQ acts on the passive layer of Al to prevent the adsorption of chloride and consequently the destruction of the native aluminum oxide film.

In this work, we investigate the influence of 8HQ and MoO₄²⁻ addition in acidic PPy electrosynthesis solution on film morphology as well as its ability to mitigate the corrosion of AA6061-T6 in the presence of chlorides.

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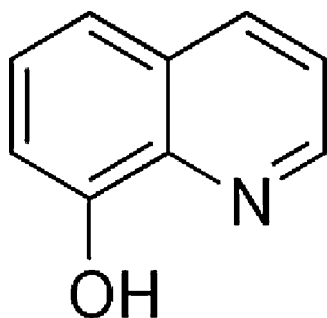


Fig. 1. Chemical structure of 8-hydroxyquinoline molecule [12].

2. Experimental

Aluminum alloy AA6061-T6 (wt.% composition: 0.15–0.40 Cu, 0.80–1.20 Mg, 0.40–0.80 Si, 0.00–0.70 Fe, 0.04–0.35 Cr, 0.00–0.15 Ti, 0.00–0.25 Zn, and 0.00–0.15 Mn) from Future Metals was used as working electrode. All specimens were 1 mm thick.

The aluminum substrates were degreased with acetone in an ultrasonic bath for 5 min, washed with distilled water and dried under nitrogen flow. The alloy samples were then masked with a mixture of beeswax and colophony resin (3:1) in order to isolate the cut edges, defining a small rectangular section of the substrate as the working electrode.

Pyrrole was distilled under reduced pressure before use. The polypyrrole films were synthesized electrochemically using potentiostatic conditions over the course of 5 min from a 0.5 M H_2SO_4 solution containing 0.5 M pyrrole (pH=0.81). The choice of the applied potential is detailed in the following section. In order to modify the polymer coating, 8HQ and Na_2MoO_4 were introduced with concentrations of 3.8 mM and 0.1 M respectively which shifted the solution pH to values of 0.91 and 1.32. Before coating synthesis, the electrolytic medium was deaerated for 5 min by bubbling nitrogen.

It is important to note that molybdate and 8HQ species were qualified acceptable to use as dopant during the electropolymerization since their protective action against corrosion was previously tested in 0.5 M NaCl solution.

The electrochemical activity of PPy films was evaluated via cyclic voltammetry in monomer-free 0.5 M H_2SO_4 solution. Morphological properties of PPy were assessed using scanning electron microscopy (Hitachi S2400).

Corrosion resistance of polymers was evaluated by potentiodynamic measurements with a potential scan rate of 1 mV s^{-1} in an aerated 0.5 M NaCl solution after an immersion period of 90 min. This exposure duration permits good reproducibility of results while also resulting in quasi-stationary conditions [14–16].

In this work, all used solutions, either for monomer electropolymerization or for corrosion tests, were prepared using Millipore water. All electrochemical methods were performed in a three electrodes-cell using a VoltaLab PGZ100 potentiostat from Radiometer. A saturated calomel electrode (SCE) was used as reference and a platinum wire as the counter-electrode. All the values of potential are referred to the SCE.

3. Results and discussion

3.1. Performance of 8HQ and MoO_4^{2-} against corrosion

Polarization curves recorded for AA6061-T6 electrodes immersed during 90 min in 0.5 M NaCl solution inhibited or not are given in Fig. 2. The shape of the anodic curves shows that the aluminum alloy substrates present a passivation phenomena

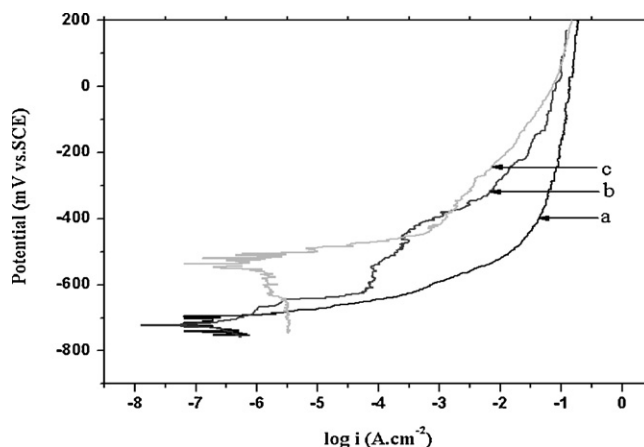


Fig. 2. Anodic polarization curves obtained for AA6061-T6 immersed during 90 min in 0.5 M NaCl: (a) undoped solution, (b) containing 8HQ; (c) containing MoO_4^{2-} ($\nu = 1 \text{ mV s}^{-1}$).

followed by a rupture of passivity by localized attack. However, electrode behavior varies as a function of medium composition.

In the absence of inhibitor, the value of the corrosion potential (E_{corr}) is about -0.71 V . It is controlled by the breakdown of the passive layer of porous aluminum oxide, due to the localized adsorption of Cl^- . Indeed, the metal surface is heterogeneous with fault zones forming, thus, active sites for adsorption and/or incorporation of chlorides in the passive film. Migrating to the substrate/oxide interface, Cl^- enables the aluminum cations hydrolysis to initiate corrosion.

The addition of 8HQ has no significant effect on the variation of corrosion potential in contrast to MoO_4^{2-} anions whose incorporation in the electrolytic medium led to a shift of E_{corr} towards a nobler value of -0.51 V . Both inhibitors pushed the pitting potential to more anodic values.

The anodic current densities recorded in the presence of dopants are the lowest. This decrease was more significant with the addition of molybdates and confirms the inhibitory action of tested species.

8HQ acts by blocking the active sites of metallic surface. It behaves as a ligand forming complex with metal ions [11–13]. As illustrated in Fig. 3, the formation of 8HQ/Al chelates inhibits the active sites of Al alloy surface.

Emregul and Aksut [17] have proposed a mechanism of oxidation/reduction to reveal the action of molybdates against corrosion of aluminum and its alloys. In fact, the dissolution of Al combined

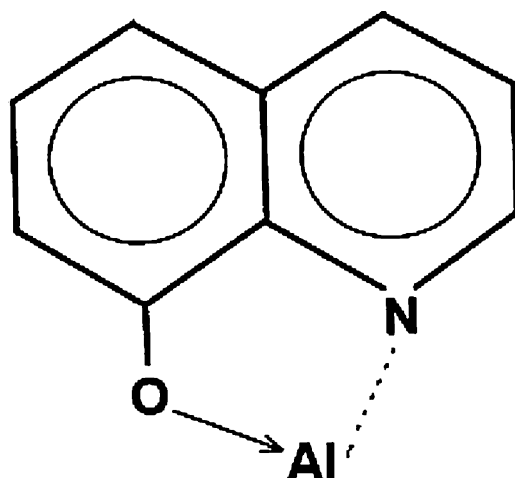


Fig. 3. Al/8HQ complex schema.

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