

# Synthesis and electrochemical evaluation of polypyrrole coatings electrodeposited onto AA-2024 alloy

M.A. Arenas<sup>a</sup>, L. González Bajos<sup>b</sup>, J.J. de Damborenea<sup>a</sup>, P. Ocón<sup>b,\*</sup>

<sup>a</sup> *Departamento de Corrosión y Protección, Centro Nacional de Investigaciones Metalúrgicas (CENIM/CSIC),  
Avd. Gregorio del Amo 8, 28040 Madrid, Spain*

<sup>b</sup> *Departamento de Química Física Aplicada, Facultad de Ciencias,  
Universidad Autónoma de Madrid, 28049 Madrid, Spain*

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## Abstract

Polypyrrole coating was successfully deposited on anodized 2024 unclad aluminum alloy showing that the presence of the anodic film is the key factor to ensure better adhesion to the polymer coating. Corrosion resistance of the conductive polymer layers grown for three and five cycles were evaluated in a 3 wt.% NaCl solution using polarization curves and impedance spectroscopy. It was found that the thermally treated polymer coating with higher thickness (five cycles) exhibited the best corrosion performance. This best coating shifts the corrosion potential towards nobler values, about 650 mV, and the exchange current density decreases two orders of magnitude regarding the anodic layer. The partial reduction of the structure of the polymer promoted by the thermal treatment plays a key role in the corrosion resistance of the coating allowing to the thermally treated polymer layer to act as a physical barrier against corrosion.

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## 1. Introduction

Initially discovered at the end of the 1970s, conductive polymers possess the electrical, electronic, magnetic, and optical properties of a metal while retaining the mechanical properties, processibility, etc. commonly associated with a conventional polymer [1]. This unique combination of properties makes them an attractive alternative to protect metals and alloys from corrosion [2]. In part, this effort has been motivated by the new environmental regulations which are forcing to replace compounds that are hazardous to human health or the environment [3]. Especially dangerous are the chromium (VI)-containing coatings currently used for corrosion control of iron and aluminum alloys. As is well known, the chromium (VI) compounds have been the main chemicals used to create conversion layers that provide better corrosion behaviour as so as to obtain a better anchorage of paints [4]. Inside this context, conducting polymers appeared as a possible replace-

ment for Cr(VI)-based coatings [5]. Conducting polymers have experienced a broad range of applications in corrosion and protection applications, from aluminum and steel to silver and copper for microelectronic industry in the last two decades [6–8].

One of the most promising applications would be related to their use as a component blended with conventional coatings (non-conductive paints) or as primer coatings because they could act – after reduction – as insulator, physical barrier.

Aluminum is an important material for use in many applications, mainly in automotive and aerospace industry due to its low density, high ductility, and good corrosion resistance. Mechanical properties are improved by alloying with many other elements, mainly Cu. However, the corrosion resistance decreases in comparison to pure aluminum.

The protection of aluminum alloys has been widely studied by many investigators using either inorganic oxidants including chromate [9], molybdate [10], and/or organic compounds having polar groups, such as oxygen, sulphur, nitrogen and heterocyclic compounds containing functional groups and conjugated double bonds [11] as corrosion inhibitors. More recently, conducting polymers have been successfully electrodeposited onto Al-2024

\* Corresponding author.

E-mail address: pilar.ocon@uam.es (P. Ocón).

alloy and the corrosion rate was reduced by about one order of magnitude [12,13].

In the present work, polypyrrole (PPy) coating was electrodeposited onto an anodized 2024 aluminum alloy. The anodising process was carried out in an aqueous oxalic acid solution. In order to deposit the PPy coating, several deposition methods were tested. The corrosion performance of the PPy coating has been studied by polarization and electrochemical impedance spectroscopy immersed in 3 wt.% NaCl.

## 2. Experimental

Specimens of 5 cm<sup>2</sup> or 3.6 cm<sup>2</sup> of 2024 unclad aluminum alloy sheet were used. Selected specimens were anodized in 0.3 M oxalic acid at 20 mA/cm<sup>2</sup> current density at room temperature for 350 s. Prior to electrodeposition, the substrate was polished using 600-grit emery paper, rinsed in Milli-Q water and ultrasonically degreased with acetone for 5 min.

Cyclic voltammetry in 0.1 M pyrrole and 0.3 M oxalic acid solution was carried out to electrodeposit coatings onto the substrate. The potential scan was performed between 0.0 V and 0.8 V. For anodized specimens, the scan was applied from 0.5 V to 1.5 V. The number of cycles was varied from three to five and the scan rate was 10 mV/s. The pyrrole was freshly distilled and stored in a N<sub>2</sub> atmosphere until its use. The reagent was stored at 0 °C in the dark. The electropolymerization was conducted at room temperature in an aerated atmosphere and non-stirred solution.

The electrodeposition process was carried out using a three-electrode cell with a stainless steel counter and Ag/AgCl/KCl (sat) reference electrode. Galvanostatic and potentiostatic were also carried out. However, the optimum adhesion and corrosion properties of the coating were obtained by the cyclic voltammetry technique. The computerised Autolab Mod. PGSTAT 30 electrochemical instrument was used as power supply.

In order to modify the polymer coating, several thermal treatments were carried out. Specimens were placed in an oven for 72 h at 35 °C, 16 h at 92 °C or performing both treatments consecutively (double treatment).

Corrosion resistance of the polymer coating was evaluated by potentiodynamic measurements and electrochemical impedance spectroscopy (EIS) in an aerated 3 wt.% NaCl solution at room temperature. A conventional three-electrode cell was employed. The reference electrode was a saturated calomel electrode (SCE) and a platinum wire as the counter-electrode.

Polarization curves were recorded after 15 min immersion in the aggressive solution starting from a cathodic potential of about –300 mV versus corrosion potential. The scan rate in potentiodynamic experiments was 0.16 mV/s.

Impedance measurements were conducted over a frequency range of 10<sup>5</sup> down to 10<sup>–2</sup> Hz, using a 3.5 mV (rms) sin amplitude.

The morphology of the coating was examined by field emission gun scanning electron microscopy (FEG-SEM) in a JEOL 6500 instrument.

## 3. Results and discussion

Polypyrrole (PPy) was electrodeposited onto Al-2024 in aqueous solution containing the monomer and oxalic acid, by using cyclic voltammetry.

The literature refers that the electrodeposited media containing oxalate ions are often used for iron and steel base materials in order to obtain a passive layer prior to electrodeposition of PPy [14]. Moreover, PPy electrodeposition using oxalic acid as electrolyte was successfully carried out on pure aluminum [15].

Fig. 1 shows the cyclic voltammograms as a function of the numbers of cycles, first and fifth, at a scan rate of 10 mV/s. It shows that the thickness of the PPy coating increases approximately with the number of cycles. Similar results were found by Iroh and Smitha Akundy [16] showing that the electrodeposition of polypyrrole on 2024 aluminum alloy in oxalic acid is higher at low scan rates. The polymer coating electrodeposited exhibits poor adhesion and areas of the substrate are not covered, as can be seen in the micrograph included in Fig. 1. Other aqueous solutions like sodium nitrate, nitric acid and sulphuric acid were also used as a growth media and similar results were found. In this sense, Saidman and Bessone showed that electropolymerization is also possible from aqueous solution like nitric acid [17] or from different salts (NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, etc.) at alkaline pH [18] but the authors reported that the PPy films had poor anticorrosion properties.

On the other hand, Martins et al. [19] indicated that other factors like surface finishing, pH and PPy concentration are also important to enhance the deposition of the polymer film.

The findings are related to the high potential applied during the PPy electrodeposition. At these positive potentials required for polymerization, the metal oxidizes and an adherent and consistent film is difficult to achieve. Literature points out that the conductive polymers film may be electrodeposited onto the surface of active metals only if the rate of anodic dissolution of these metals is reduced. It can be achieved by passivation of the

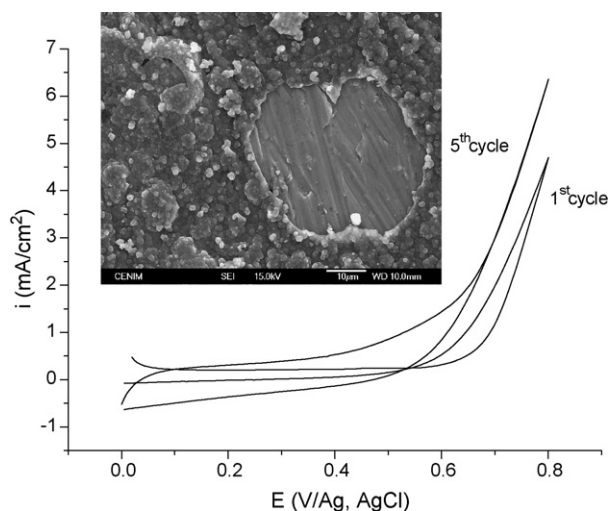


Fig. 1. Cyclic voltammogram for 2024 aluminum alloy in a 0.3 M oxalic acid and 0.1 M pyrrole solution at a scan rate of 10 mV/s. SEM image of the surface appearance after deposition of the polymer coating is inserted.

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