

## Corrosion Protection of Aluminum and Aluminum Alloys by Polyanilines: A Potentiodynamic and Photoelectron Spectroscopy Study

A. J. Epstein<sup>a,b</sup>, J. A. O. Smallfield<sup>b</sup>, H. Guan<sup>a,b</sup>, and M. Fahlman<sup>b</sup>

<sup>a</sup>*Department of Physics, The Ohio State University, Columbus, Ohio 43210-1106*

<sup>b</sup>*Department of Chemistry, The Ohio State University, Columbus, Ohio 43210-1173*

### Abstract

Corrosion protection capabilities of polyaniline in the emeraldine base form and self-doped sulfonated polyaniline form have been studied for aluminum and Al 3003 and Al 2024-T3 alloys. The polyaniline is applied as a coating on the aluminum coupons which were exposed to a variety of corrosive environments, including 0.1M NaCl. The oxide layers that formed were studied by X-ray photoelectron spectroscopy depth profiling using argon sputtering. Potentiodynamic polarization studies were used to determine changes in corrosion current and corrosion potential as well as pitting potential. For Al and Al 3003 there were modest indications of potential corrosion protection capability of polyanilines. The coatings of emeraldine base (EB) and sulfonated polyaniline (SPAN) on Al 2024-T3 were effective at reducing the corrosion rate when these coated coupons were exposed to 0.1M NaCl environment. The XPS study suggests a reduction in the copper concentration at the surface of the coated coupons. It is suggested that the EB and sulfonated polyaniline coatings facilitate the extraction of copper from the surface of the Al 2024-T3 thereby reducing the galvanic couple between aluminum and copper that usually leads to accelerated corrosion for the Al 2024-T3 alloys.

*Keywords:* polyaniline, sulfonated polyaniline, corrosion, aluminum

### 1. Introduction

The corrosion of metals has long been a problem to society and hence is an important area of research. Although aluminum forms a protective aluminum oxide layer on the surface, this coating can be breached in aggressive environments leading to corrosion. In particular, NaCl containing environments lead to the formation of aluminum chlorides which in turn reduce the effectiveness of the oxide layer in preventing corrosion. The presence of 4–5% copper in Al 2024-T3 alloy is a particular problem as this introduces a galvanic couple between the aluminum and the copper thereby accelerating corrosion. The 2024-T3 is an alloy used in aircraft applications where its increased strength adds value to the aluminum structures. It is important to develop coatings which contain heavy metals and protect the aluminum against rapid corrosion.

It has been shown in earlier studies [1–11] that doped polyaniline provides some effectiveness against corrosion of iron and steel. The mechanism for corrosion protection of emeraldine base and sulfonated polyaniline on the iron and cold rolled steel was shown to be due to charge transfer from the iron/steel to the polyaniline. The reduction/oxidation model is described in reference 10. It was shown that emeraldine base has a substantial throwing power when used as the coating for cold rolled steel and other iron based materials [4,10].

Initial studies of a double strand of polyaniline and a polyanion suggested that this composition provides some corrosion protection for aluminum AA7075 alloy [12]. The studies were carried out in a NaCl solution. In contrast, a recent study of camphor sulfonic acid doped polyaniline coated on Al 2024-T3 suggests that this form of polyaniline was not effective at reducing corrosion when the coated material is exposed to a 3.5% NaCl solution [13]. We present here the

results of a study of an X-ray photoelectron spectroscopy (XPS) and correlated potentiodynamic polarization studies for emeraldine base and also sulfonated polyaniline coated Al, Al 3003, and Al 2024-T3. The results suggest that under some conditions polyaniline can reduce corrosion rates for Al and its alloys. In particular, reduced corrosion rates and fewer corrosion products were observed for Al 2024-T3 coated with EB or crosslinked SPAN. A mechanism is suggested for protection of copper containing aluminum alloys through removal of copper from the surface of the corroding alloy thereby reducing the corrosion rate.

### 2. Experimental Details

Polished (600 grit) Al 2024-T3 and Al 3003 coupons were prepared and ~20 microns thick EB films were dropcast from 20mg/ml N-methylpyrrolidinone (NMP) solution. Other coated Al 2024-T3 coupons were also prepared by first spin coating ~2000Å thick insulating polymer on the surface. Sulfonated polyaniline was spun from a solution and crosslinked to the other polymer. The Al 2024-T3 samples used for XPS studies were immersed in 0.1M NaCl solution, kept at room temperature for 10 hours to 66 hours. Prior to insertion into the ultra-high vacuum chamber, the polymer films were removed by lifting up on the corner. A VG Scientific ESCALAB MkII XPS spectrometer with Mg K $\alpha$  X-rays (1253.6eV) was used for the XPS studies. This pressurized system was ~10<sup>-9</sup> mbar. Sputtering for the depth profiling experiments were carried out using a 5.5 keV Ar ions, using a sputtering rate of ~25Å/min. For the electrochemical experiments, polymer coated and uncoated Al 2024-T3 coupons were placed in the holder at the bottom of a vessel with the coated side exposed to the 0.1M NaCl solution. The coated and uncoated Al 2024-T3 coupons

Table 1. Potentiodynamic Measurements of Various Coating Samples

Samples	Pitting Potential (mV)	Corrosion Potential (mV)	Corrosion Current Density (A/cm <sup>2</sup> )
Bare Al 2024-T3	~ - 600	~ - 990	~ 7 × 10 <sup>-8</sup>
EB coated Al 2024-T3	×	~ - 480	~ 7 × 10 <sup>-9</sup>
SPAN coated Al 2024-T3	×	~ - 880	~ 8 × 10 <sup>-9</sup>

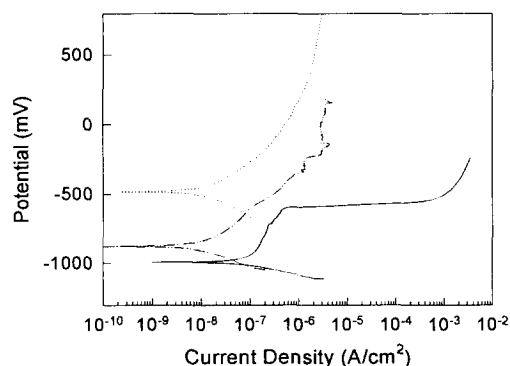


Figure 1. Potentiodynamic scan of bare Al 2024-T3 (—), EB coated (···), and SPAN coated (---) Al 2024-T3 Coupons.

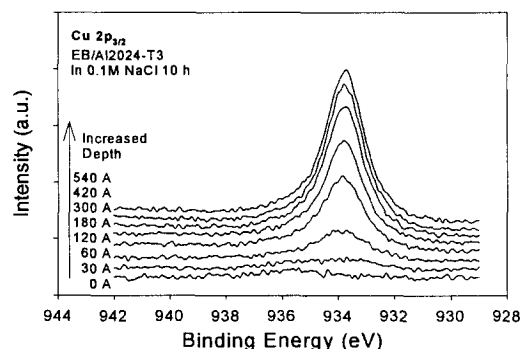


Figure 3. XPS depth profiling of EB coated Al 2024-T3 after exposure to 0.1M NaCl for 10 hours.

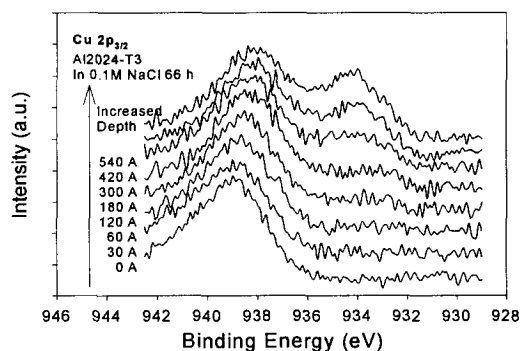


Figure 2. XPS depth profiling of bare Al 2024-T3 after exposure to 0.1M NaCl for 10 hours.

functioned as working electrodes in the three electrode set up. A platinum foil was used as a counter electrode and a saturated calomel electrode (SCE) was used as a reference. The potentiostat used for the potentiodynamic experiments was a Gamry Instruments model PC3 Potentiostat/Galvanostat equipped with the CMS 100 corrosion system software. The scanning speed for the experiment was 5mV/s and the coupons were exposed to electrolyte for 10 minutes prior to data acquisition.

Emeraldine base was drop cast from NMP solution onto Al 3003 coupons. The coated coupons were exposed to a 0.1 M HCl bath at 80°C for 2 hours, followed by XPS studies on the side opposite to EB coated side.

Aluminum films (>100 nm) were evaporated onto a thick EB films formed by drop casting onto glass. These thin films were exposed to HCl vapors followed by XPS studies.

### 3. Results and Discussion

The XPS studies of the backside of EB coated Al 3003 and Al evaporated on EB showed a modest reduction of the oxidized aluminum 2p peak at a depth of 65 nm (as compared to the metallic aluminum 2p peak) supporting the possibility of corrosion protection of aluminum. Studies then focused on the copper rich Al 2024-T3 systems. After immersing the coated and uncoated aluminum Al 2024-T3 in 0.1M NaCl solutions for either 10 or 66 hours, severe corrosion was observed on uncoated coupons while the coated coupons showed less corrosion. Typically the corrosion current measured for the coated coupons was tenfold reduced from that of the uncoated materials indicating much lower corrosion rates, Figure 1 and Table 1. XPS studies showed dramatically less corrosion products on the surface. Of particular note was the XPS study showing the absence or reduced concentration of copper in the top several hundred Å of the Al 2024-T3, Figures 2 and 3. As a result we suggest a model in which the sulfonated polyaniline or emeraldine base plays a role in dissolving away the copper containing corrosion products. This would play a key role in eliminating the presence of a galvanic couple between the aluminum and copper thereby dramatically reducing the corrosion rate.

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