Corrosion inhibition on a aluminum alloy by an acrylic conducting blend

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The use of intrinsically electronically conducting polymers (ICPs) for corrosion protection was first reported by Mengoli *et al.*[1] in 1981 and again in 1985 by DeBerry.[2] In the latter case, electrodeposited polyaniline (PANI) was used for corrosion protection of steel in strong acid media. Since these early reports, there has been increasing attention on the use of ICPs in corrosion protection of different metals. Kinlen *et al.*[3] provided spatially resolved information on the redox processes occurring in the polymeric layer using the scanning reference electrode technique (SRET). He proposed a mechanism in which the PANI film maintains the potential of the metal substrate in the passive region, leading to passivation of newly exposed metal surfaces.

Recently was showed[4] that the counter-ion of the cationically charged ICP can play an important role in the passivation mechanism. Specifically, that study showed that galvanic coupling between the PANI and the metal, such as might be produced when the PANI film/metal interface is mechanically damaged, leads to local reduction of the PANI film. This drives expulsion of the counter-ion, which then becomes available to complex any  $Fe^{2+}$  or  $Fe^{3+}$  species that might be released during corrosion of the metal surface. For cases in which the anion forms a tight complex with one or more of the released metal species, this process can lead to deposition of a second passivating film.

Electrochemical experiments were performed in a conventional three electrodes Pyrex<sup>®</sup> cell using aluminium alloy, A2024 sheets ( $\phi$ =0.5 cm) as working electrodes, a platinum sheet as counter electrode and all potentials were referred to the saturated calomel electrode (SCE). All experiments were performed at room temperature and all chemical used were A.R degree. Polyaniline (PANI) blends were prepared following the procedure already described in the literature [5]. Raman Spectroscopy was used to follow the oxidation changes in the system by the utilization of a Renishaw Raman Imaging Microscope System 3000 with an Olympus metallurgical microscope, a CCD detector and a He-Ne laser ( $\lambda_0 = 632.8$  nm, Spectra Physics mod.127) as the exciting radiation. Scanning electrochemical microscopy (SECM) (CHI900 Electrochemical Workstation) was used to follow the formation of the second passive layer. This method has been used previously to examine oxide defects at Al and other metal surfaces[6].

Figure 1 shows the open circuit potential ( $E_{oc}$ ) as a function of time for two different electrodes: naked A2024 electrode (-0,76 V) (full square), A2024/PMMA (open circles) and A2024/PMMA-20% PANI-CSA (full circles) in 10<sup>-3</sup> molL<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution. The protective character of the conductive coating is clearly shown in the figure by the stabilization of potential at *ca.* –0.15V during 100 days. The relevant role played by the conductive phase (PANI-CSA) in the blend is also demonstrated in the figure by considering the curve obtained with the Fe/PMMA interface that, after few hours in acidic media, the potential evolves to the value corresponding to A2024 active behavior. By using SECM the formation of a second protective layer formed on the bare surface exposed by producing a scratch on the surface was follow. These experiments clearly show that the complex CSA-Al has a protective character.

Another important fact is that, the attainted open circuit potential is not so far from the corrosion potential of A2024, the presence of PANI in the blend enhances the protective character of the coating. Raman spectroscopy also shows the formation of a camphosulfonate – aluminum complex as a second protective layer and the reduction of polyaniline in the blend provoques the redox reaction between polyaniline and aluminum.

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**Figure 1** – Open circuit potential as a function of time for ( $\blacksquare$ ) naked A2024 electrode, (O) A2024/PMMA electrode, and (●) A2024/PMMA-PANI-CSA electrode in 10<sup>-3</sup> molL<sup>-1</sup>H<sub>2</sub>SO<sub>4</sub> electrolytic solution.