

STABILIZATION OF IRON PASSIVITY USING DIFFERENT ANILINE COPOLYMERS

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We showed that a conductive polymer such as polyaniline (PANI) could play an important role in the protection of iron against corrosion, by stabilizing the passive layer. It can therefore be efficient only when the passive layer itself presents a high quality, which can be obtained by polymerizing PANI in phosphoric solution after a first step of passivation without aniline [1]. We showed that the protection time could be largely enhanced when a copolymer (SPANI) containing aminobenzene sulfonic units was formed [2]. The electron spectrum of SPANI is different, displaying the presence of free-carriers (bipolarons are never formed) in a large potential range, in the same time as the existence of a second kind of oxidized units [3]. Recently, Raman studies showed that the particular behavior of SPANI could be assigned to a cross-linkage by the sulfonate groups rather than to "self-doping" [4].

To understand the role played by the substituent present on the benzene ring and be able to relate it to the improvement of protection, we studied another polymer: poly ortho-methoxyaniline (POMA). The interest of testing this substituent is that it is an electron donor, while sulfonate is an electron acceptor. The optical spectra of films electropolymerized from a phosphoric solution on platinum and studied during their polarization in pH 2 K_2SO_4 medium (figure 1) display this large difference: bipolaronic form (band at ≈ 1.5 eV) is present in almost the whole potential range; excitonic absorption at 2.35 eV, characteristic of exchange in substituted rings, appears at -200 mV/SSE, (instead of $+250$ mV/SSE in PANI) showing the easy oxidation of this polymer. A large amount of free carriers (band at ≈ 1 eV) are also detected.

Raman spectroscopy is used in parallel; the spectra of POMA electropolymerized on iron are in particular collected at different times during and after the breakdown. In the preliminary Raman spectra shown here, the films are polymerized from oxalic acid solution and studied in a pH 3 K_2SO_4 medium. Such as in the case of SPANI, two different amine vibrations at 1260 and 1205 cm^{-1} (the later corresponds to nitrogen which is perturbed by the substituent) are detected. The value of $\nu(C=N)$: 1500/1510 cm^{-1} corresponds to a strong charge borne by imine function in reason of the presence of substituent. A band assigned to the cross-linkage is present at 1440 cm^{-1} (a wavenumber higher than in SPANI). $\delta(C-H)$ is at 1125 cm^{-1} , a very low value with respect to PANI. In general, the wavenumber shifts are higher in POMA than in SPANI, which suggests a larger chain perturbation.

In figure 2, obtained with a laser red excitation (632 nm) one can see that the two substituted polymers remain strongly protonated after the breakdown. The differences will be discussed in connection with the protection properties, characterized by the time during which the ocp potential remains at its passive value.

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 [2] M.C. Bernard, S. Joiret, A. Hugot- Le Goff, P. V. Phong, *J. Electrochem. Soc.*, (2001), 148, B304
 [3] M.C. Bernard, S. Joiret, A. Hugot- Le Goff, P. D. Long, *J. Electrochem. Soc.*, (2001), 148, B299
 [4] M.C. Bernard, A. Hugot- Le Goff, S. Joiret, unpublished results

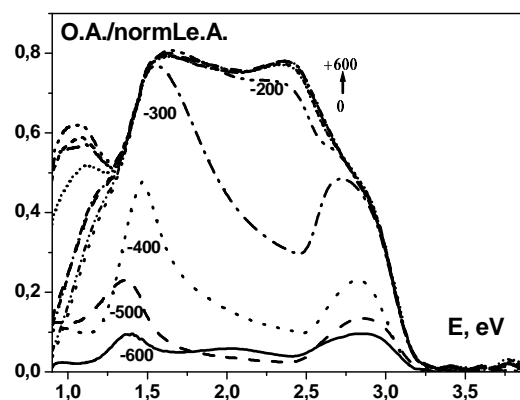


Figure 1 Optical absorption of POMA films on Pt (K_2SO_4 , pH 2) normalized by the leucoemeraldine spectrum. Potential measured vs SSE.

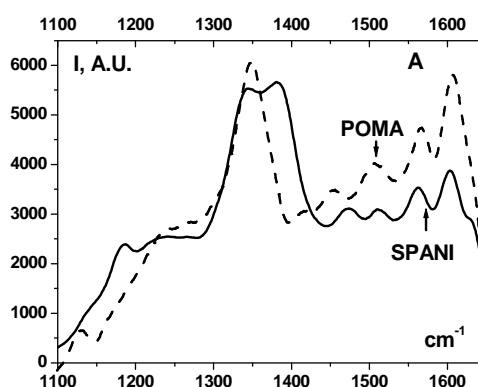
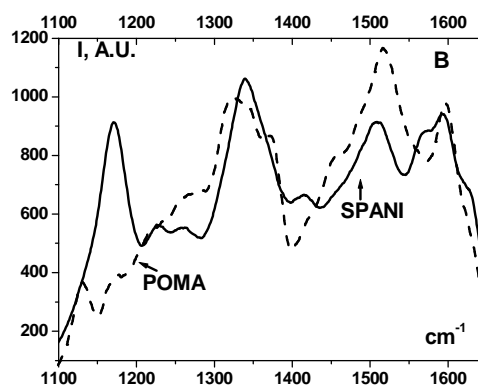


Figure 2 Raman spectra of films polymerized on iron, measured in K_2SO_4 , pH 3 before (B) and after (A) breakdown