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Corrosion resistance and antibacterial activity of electrosynthesized polypyrrole

A. El Jaouhari[a,*], A. El Asbahani[a,c], M. Bouabdallaoui[b], Z. Aouzal[b], D. Filotás[d,e], E.A. Bazzaoui[b], L. Nagy[d,e], G. Nagy[d,e], M. Bazzaoui[a], A. Albourine[a], D. Hartmann[c]

[a] Equipe de Chimie de Coordination, Laboratoire des Matériaux et Environnement, Faculté des Sciences, Département de Chimie, Université Ibn Zohr, B.P. 8106, Agadir, Morocco
[b] Faculté des Sciences, Département de Chimie, Université Mohammed Ier, 60000 Oujda, Morocco
[c] Laboratory of Microbiology, Equipe I2B, Département Pharmaceutique de Santé Publique, ISPB, Faculty of Pharmacy, University Claude Bernard–Lyon 1, Lyon, France
[d] Department of General and Physical Chemistry, Faculty of Sciences, University of Pécs, Ifjúság útja 6, 7624 Pécs, Hungary
[e] János Szentágothai Research Center, University of Pécs, Ifjúság útja. 20, 7624 Pécs, Hungary

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ABSTRACT

In this work, we describe a method for coating a carbon steel surface by (PPy) layers to improve its corrosion resistance capabilities and also these antimicrobial properties. The coating was obtained by electrosynthesis in the sodium salicylate solution using cyclic voltammetry and galvanostatic techniques. Surface analysis by XPS, SEM and Raman spectroscopy confirmed the electrodeposition, stability and morphology of (PPy) film on the carbon steel surface. The corrosion protection properties of the coatings were examined by OCP, EIS and atomic adsorption spectroscopy revealing a high degree of corrosion-resistance in salt containing medium. The antibacterial activity of the modified surface was assessed by using the standardized method ISO 22196 confirming enhancement of the antibacterial activity of this coated material comparing the untreated surface to the Silver/PPy coated carbon steel. This coated carbon steel material acquired interesting qualities of corrosion resistance, low cost and antibacterial for many industrial applications.

1. Introduction

Among all metal alloys, carbon steels, remain the most commonly used materials in large tonnage in several domains and industrial applications including transport and equipment (automotive and rail), marine, chemical and metal processing, canalization and construction because of their good performance/price ratio [1]. They offer a wide spectrum of use properties resulting from their mechanical characteristics, which are closely related to their microstructure and composition, thus making them with great interest due to the low cost. However, Carbon steel and its alloys are easily corroded and are vulnerable particularly to pitting corrosion in electrolyte solutions containing halides such as chloride ions [2] and this is one of the major disadvantages limiting their uses. Different strategies can be used to achieve protection of carbon steel from corrosion. The use of organic compounds, such as propargyl alcohol, aminotriazole, benzotriazole and several Schiff bases is well known and has been widely reported [3–5]. Although, these excellent inhibitors are suitable for various media, their toxicity is a serious problem limiting their uses. Consequently, many recent researches focused on the development of new, safe and eco-friendly processes particularly coating by using the polymers as protecting agents [6,7].

These latter were long considered insulating materials and were used as such in electrical conduit, clothing and packaging. However, the Nobel Prize in Chemistry 2000 was awarded jointly to A.J. Heeger, H. Shirakawa and A.G. MacDiarmid for the discovery and development of electrically conductive polymers [8]. This has opened a large panel of applications of this kind of polymers in materials sciences and extended their scope of use to many domains and applications (such as corrosion inhibitors) and demonstrate their utility to the scientific community [9–11].

Several research studies have been conducted on the ability of these polymer coatings to protect oxidizable metals against corrosion. Indeed Herrasti et al. [12] have demonstrated the

* Corresponding author.
E-mail address: abdelhadi.eljaouhari@edu.uiz.ac.ma (A. El Jaouhari).

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protective effect of polypyrrole films against corrosion of stainless steel, by moving the corrosion potential to more positive values and reducing the corrosion current. This type of protection is based on a mixed mechanism of isolation and load transfer [13,14]. Recently, a broader concept based on anion exchange through the polymer backbone, has been reported to explain the passivation of the metal surface [15–17]. Kowalski et al. [18] have prepared a double layer of polypyrrole on carbon steel. This bi-layers system shows a good behavior against corrosion. In this system the first layer is doped with ($PMo_{12}O_{40}{}^{3-}$) and ($HPO_4{}^{2-}$) and the second layer by dodecyl sulfate ions (CH_3 $(CH_2)_{11}OSO_3{}^{-}$). This coating presents a new polymer capacity approach to repair the artificial structural defects, and consequently a renaissance in the passive state of the metal substrate. Indeed, the outer layer is sufficiently stable in the polymer matrix to form a membrane that acts as a selectively permeable barrier for migration of small anions or of the inner layer or from the corrosive environment. This provides an electrochemical barrier to the penetration of halide anions such as Cl^- responsible for the degradation of the passive layer. Similarly, the ion selectivity of the outer layer causes mobility of $MoO_4{}^{2-}$ anions that are trapped in the inner layer, which simply means that they can be consumed in the interfacial process of Fe/Ppy regenerating the passive film.

Moreover, several authors report the application of conductive polymers coatings to obtain surfaces having antibacterial activity. González et al. [19] suggest a deposit of silver on polypyrrole doped by salicylate ions to inhibit the Gram-positive bacteria *Staphylococcus aureus* (S. aureus). They explained this activity by the penetration of the released Ag^+ ions and colloid silver particles through the bacteria cell wall. The complexation with enzymes of the bacteria conducts to the inhibition and consequently to the bacteria death. Fernando et al. [20] also studied the influence of morphology and additives incorporation on antibacterial activity of branched (Ppy). The process of antibacterial activity is favored by electrostatic interaction established between positive charges of polypyrrole nanoparticles and bacterial cell wall (charged negatively). It was attributed to the size of polymer nanoparticles [20]. It was observed that the concentration of the salicylate can affect the morphology of the forming layer, namely in case of higher salicylate concentration rectangular microtubes are forming while at lower salicylate level (e.g. 0.1 M), the PPy shows the regular, granular morphology [21]. The better corrosion resistance of the latter was also demonstrated. Cysewka et al. showed the lowering of the salycilate concentration in the electrolyte result wider potential window [22].

In the present work, we focused on the use of (Ppy) layer as coating material to enhance the corrosion resistance of carbon steel. For improving the antibacterial properties of our materials, we chose the chemical deposition of silver layer on the (Ppy) one to induce antibacterial activity. Due to the fact that some bacteria can tolerate saline environments such as *Staphylococcus aureus*, we decided to cover the layer of polypyrrole by another of silver to render them antimicrobial in such environments. The antibacterial activity of the obtained coated metal surfaces was evaluated by using the ISO 22196 standardized method. For that, we intentionally used a *staphylococcus aureus* strain because of its well-known tolerance to saline medium and it was considered as one of the most important markers of general infection control standards [23]. *Staphylococcus aureus* is also known for its highly invasive capacities and involvement in the colonization and contamination of surfaces, materials and substrates such as medical devices and implants particularly in the presence of iron [24]. Contrary to quantitative assessment methods, the ISO 22196 standard allows the quantification and comparison of the antibacterial activity of various surfaces which allow determining the most active between them.

2. Experimental

2.1. Electrochemical cell and chemicals

All electrochemical measurements were performed using a conventional three-electrode cell connected to Voltalab PGZ301 potentiostat controlled by VoltaMaster 4. The working electrode used in this work is a carbon steel ($2\,cm^2$) of JIS G3131 SPHC specimen which composition is C: 0.04%, Mn: 0.15%, P: 0.026%, S: 0.005%, and Si: 0.02%. Before each use, the working electrode is polished mechanically with 600, 800, 1000 and 1200 abrasive paper, and rinsed several times with distilled water and acetone. The auxiliary electrode is a stainless steel plate. and a Ag/AgCl (KCl 0.1 M) electrode was used as reference.

Pyrrole was distilled prior to use while sodium salicylate and NaCl (>99%) were used as received (Merck).

The EIS measurements were carried out to an open circuit potential with a 10 mV in amplitude of the superimposed AC signal, and the applied frequency were between 100 kHz and 10 MHz. The EIS curve fitting was accomplished using Zsimpwin software. Electrochemical corrosion measurements were performed at room temperature in 3% NaCl solution.

The deposition of silver on the polypyrrole coated was performed by immersing the coated electrode in a 0.05 M of $AgNO_3$ solution under dark conditions and open circuit potential for 3 h.

2.2. Instrumentation

2.2.1. SEM analysis

The scanning electron micrograph of all samples was analyzed using JOEL Ltd., JXA-8900 instrument. The pressure of the microscope chamber was maintained between 4 and 10 Pa.

2.2.2. XPS analysis

The X-ray photoelectron spectroscopy (XPS, Shimadzu Co: AXIS ULTRA) instrument was used for specimen surface compositions with X-ray source of Mg K operated at 15 kV and at anodic current of 10 mA, The analysis area was 2 mm × 1 mm.

2.2.3. Raman analysis

The Raman spectra of polypyrrole coating were taken using Horiba Jobin Yvon Raman DU420A-OE-325 Spectrometer in the range 2000–200 cm^{-1}.

2.2.4. AAS analysis

PerkinElmer PinAAcle 900T atomic absorption spectrometer controlled by WinLab32™ for AA software was applied in FAAS iron content measurement. The analyses were carried out in 1% HNO_3 solutions of 0–5 ppm Fe, with 0.12 ppm as LDL.

2.3. Antibacterial assays

The antibacterial activity of the activated metal area was determined according to the ISO 22196 method. Briefly, a 2.5×10^5 UFC/mL inoculum of *Staphylococcus aureus* (CIP 4.83 strain) was prepared in a 1/500 diluted Muller-Hinton Broth from 18 h culture. Surface area of activated and non-activated metals ($5 \times 5\,cm^2$) were inoculated with 400 μL of the inoculum and covered with a ($4 \times 4\,cm^2$) para film. The viable number of bacteria on the different studied surfaces (Silver activated metal, non-activated metal, polypyrrol deposited metal and glass as control) was determined in duplicate after 0 and 24 h of incubation. Bacteria were recovered from the different surfaces by the mean of Stomacher bags containing neutralizing diluent pharmacopoeia. Viable number of bacteria was determined after serial dilutions