

The Influence of Oxidizing Agent in the Chemical Deposition of Polypyrrole on Lead Alloy Surface

Inês Moreira Vilanova Pinheiro¹ & Liu Yao Cho^{1,2}

¹ Research and Development Institute, Paraíba Valley University - UNIVAP, São José dos Campos, SP, Brazil

² Faculty of Engineering, Architecture and Urbanism, Paraíba Valley University - UNIVAP, São José dos Campos, SP, Brazil

Correspondence: Liu Yao Cho, Organic Electrochemistry Laboratory, Research and Development Institute of Paraíba Valley University - UNIVAP, Av. Shishima Hifumi 2911, São José dos Campos, SP, Brazil. E-mail: liu@univap.br

Received: October 17, 2019

Accepted: November 27, 2019

Online Published: December 5, 2019

doi:10.5539/jmsr.v9n1p1

URL: <https://doi.org/10.5539/jmsr.v9n1p1>

Abstract

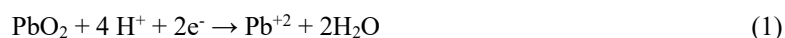
Polypyrrole (PPy) layers were deposited on lead metallic surface using hydrogen peroxide or benzoyl peroxide as oxidizing agent associated with different types of dopants: phosphoric acid, stearic acid and dodecylbenzene sulfonic acid. Lead alloy was chosen because of its importance in energy industrial application and also because its primary source of extraction is running out, there is an increasingly urgent need to extend its life cycle. For the *in situ* chemical deposition of PPy, it was considered the combination of only one oxidizing agent and one dopant, being the experiment performed with the combination of these reagents. The morphology and corrosion protection effectiveness of the PPy layer was studied by Scanning Electron Microscope (SEM), Open Circuit Potential (OCP) and Potentiodynamic Polarization. The experimental results demonstrate that PPy layer was effectively formed as a coating layer and Hydrogen Peroxide performed better and consistent protection efficiency when compared to Benzoyl Peroxide.

Keywords: chemical deposition, polypyrrole, lead alloy, oxidizing agent, dopant

1. Introduction

Lead and its alloys have been widely used in many types of industries, from cable sheaths to radiation shielding and it is still a major raw material in the automotive battery industry. However, the use of lead for these applications has now been taken over by other less toxic and cheaper alternatives (Yang et al., 2017). The industrial use of lead metal and its alloys inspires caution as lead is a cumulative toxic substance that affects many body systems and is particularly harmful to young children (Pearson & Schonfeld, 2003). The primary mineral source of lead should be depleted within the next 100 years (Casas & Sordo, 2006) and the proportion of lead produced from secondary sources (i.e. scrap metal), which represents about 60% of total worldwide production, is also higher in the more industrialized countries. Western Europe produces 60% of its lead from secondary sources, while the US owns about 70% from secondary sources, of which 94% comes from waste lead acid batteries (Thornton et al., 2001). The development of the automotive industry drives the rapid cycle of consumption and disposal of these batteries, which requires high market demand for the finished product and consequent sources of raw materials generating an ever-increasing spiral of demand and production (Recycling Economy, 2017; Xiao, 2012). Secondary production requires much less energy than producing lead from ore, primary production 7,000-20,000 MJ/t lead, secondary production 5,000-10,000 MJ/t lead (Thornton et al., 2001).

Lead alloy oxidizes very easily even when in contact with thin air and the lead dioxide (PbO₂) generated from this oxidation is a substance that holds tendency to receive electrons. Metallic lead (Pb⁰), on the other hand, has a great tendency to donate electrons. Therefore, when both are in contact there will be the transfer of electrons from lead to lead dioxide (Diniz, 2004). The reactions that happen in the corrosive process of the metallic substrate being the reactions in the cathode (1) and anode (2):



The corrosive process acts as an energy generator, since there is a decomposition of the metallic substrate by electrochemical or chemical reaction, usually in aqueous environment, where the factors that interfere in the kinetics of the corrosion reaction are, among others, temperature, concentration of electrolyte, the type of metallic substrate used and the overall operating conditions of the process (Sousa, Lima, & Vilar, 2016). The corrosion protection of metals and alloys by using conducting polymer coating has been emerged as a feasible alternative and have revolutionized material science as they can be used in single parts or deposited in finely homogeneous layers, assuming the required shape regardless of geometry, easy and generate gain without increasing the efficiency of the electric current. Polypyrrole (PPy) is non-toxic, have high electron conductivity, anti-corrosive property, good adhesion to the grid surface making it suitable for the present application (Gurunathan et al., 1999; Holze & Wu, 2014; Garcia & Smit, 2006). Intrinsically conductive polymers have been widely applied in corrosion protection due to their high protection effectiveness, relatively low cost and their low impact on the environment (Lei, 2014). The conductivity that is inherent in a conductive polymer is due to the doping process that can occur during its synthesis, which is accompanied by the incorporation of anions present in the electrolyte used (Tallman De et al., 2002). Conductive polymers are materials that have electrochemical activity and their use is possible in a wide range of applications, such as sensors, energy accumulators, electrodes, etc (Ameer & Adeolu, 2005). Many studies have shown that PPy films can also be used to protect oxidizable metals against corrosion (Tallman De et al., 2002). PPy has high stability, it is easy to polymerize by chemical or electrochemical process and it can be synthesized in aqueous medium containing various electrolytes, which can be incorporated into the polymer chain and modify the conductive properties of the film (Tallman De et al., 2002). It is known that there are ways to improve the effectiveness of protecting polypyrrole coatings. One is the use of dopant at the time of polypyrrole synthesis with different anions, especially those that are bulky, have long carbon chains and result in deposited layers with superior anti-corrosion performance compared to those doped with less bulky substances. Larger anions will be trapped within the polymer molecule, making it difficult to exchange with aggressive chloride ions from the corrosive medium (electrolytes). Conductive polymers may also act as a reservoir of inhibiting anions. (Eslami et al., 2019) Regarding the state of the art of the theme addressed in this study, it is observed that references on "Chemical and electrochemical deposition of polypyrrole on lead alloy surface" are scarce (Eftekhari & Ahmadi, 2006). Regarding deposition on metallic substrates such as magnesium, copper, aluminum, zinc, stainless steel, there is a good database previously published (Menkuer & Ozkazank, 2019; Vera et al., 2014; Sheng et al., 2014; Mortazavi et al., 2019; Samad et al., 2019; Sharifirad et al., 2010; Annibaldi, Rooney, & Breslin, 2012; Ferreira, Liu, & Cho, 2018; Souza, Liu, & Cho, 2018; Liu, Bezerra, & Cho, 2017).

In this paper, we studied the influence of the oxidizing agent and its influence among the PPy chemical deposition process on lead alloy surface. Chemical deposition of the PPy polymer was performed *in situ* on the metallic substrate using a one-step process that is relatively controllable from the combination of oxidizing and doping agents' solutions. PPy layer formed morphology was analyzed by the Scanning Electron Microscopy (SEM). The effective performance of the deposited layers was evaluated using the electrochemical analysis open circuit potential (OCP) and Potentiodynamic Polarization.

2. Experimental

The lead alloy samples (Weight%: Pb=84.73%, O=6.45%, Sn=3.69%, Bi=2.10%, Ir=1.76%, Zn=1.27%) were disc-cut with 2.0 cm diameter surfaces, sanded with 220, 400, 600, 800 and 1200 grit size sandpaper. The last step of the mechanical treatment of the samples was to use alumina felt. The samples were then rinsed with distilled water and dried completely before each chemical deposition.

Chemical depositions on sample surfaces were performed using the *in situ* deposition technique and the reactions occurred at controlled temperature (40°C) with Pyrrole monomer (C_4H_5N , Aldrich). Each sample was prepared with a combination of one oxidizing agent and one dopant, following the Table 1. The oxidizing agents used were hydrogen peroxide (V30, Synth) or benzoyl peroxide ($C_{14}H_{10}O_4$, Dynamics) and the dopants used were phosphoric acid (H_3PO_4 , Merck), DBSA (dodecyl benzene sulfonic acid, $C_{18}H_{29}NaO_3S$, Aldrich) and stearic acid ($C_{18}H_{36}O_2$, Aldrich).

After mechanical treatment with the grit sandpaper, the samples were submerged in ethanol and water (7:3, respectively), oxidizing agent and doping solution for 15min. Afterwards, the discs were submerged in another prepared solution containing ethanol, water (7:3) and 0.2 mol.L^{-1} of the pyrrole monomer and rested for 60 minutes. After this time, the remaining hydrogen peroxide was transferred to the solution containing pyrrole with the lead alloy disk. The reaction was under controlled heating at 40°C for 72 hours to ensure complete coverage of the conductive polymer on the metal sample. After this time, the samples were carefully removed from the reaction medium and submerged in distilled water 3 times, rinsed and dried under vacuum.

Table 1. Design of experiments composition

Samples		
Monomer	Oxidizing agent	Dopant
Pyrrole	Hydrogen peroxide	H ₃ PO ₄
		DBSA
		Stearic acid
	Benzoyl peroxide	H ₃ PO ₄
		DBSA
		Stearic acid

The roughness of the metal discs after the *in situ* chemical deposition of the polypyrrole was determined by the INSIZE model ISR-16 portable digital roughness meter.

Electrochemical analysis was performed using a Potentiostat / Galvanostat (Model MQPG-01 Microquimica) in a one-compartment cell containing three electrodes being performed at 25°C. The working electrodes were embedded with Teflon[®], lead with 0.53 cm² disk-exposed area. The reference electrode was a saturated Ag/AgCl electrode and the auxiliary electrode was a 5cm long platinum stick. The protection against corrosion of lead alloy samples covered by PPy films was investigated by potentiodynamic polarization curves in 0.1mol.L⁻¹ NaCl Solution (pH = 6), which was neither stirred nor opened to the atmosphere and maintained at room temperature of 25°C. Analyzes were performed by varying the electrode potential at 1.0mV/s from -1.0V to +1.0V and reversing the potential to -1.0V. The potential and density of the corrosion current were obtained using the Tafel Curve.

The morphology of surfaces coated with the Polypyrrole films was analyzed using a Zeiss Scanning Electron Microscope (SEM) EVO 10-07-47, Secondary Electron model (SE). The micrographs were obtained using a 20keV electron beam.

3. Results and Discussion

3.1 Chemical Deposition of Polypyrrole (PPy) on Lead Alloy

From the results of PPy chemical deposition, a consistent, adherent and homogeneous PPy coating layer was obtained directly on the polished surface of each sample, using the 0.2 mol.L⁻¹ pyrrole monomer and the combination of each oxidizing agent with only one dopant. The activation of the metal substrate with the oxidizing agent favors the nucleation of PPy on the surface of the lead alloy, forming the polymer layer. Figure 1 shows the SEM micrographs of the lead alloy surfaces coated with PPy layers, using hydrogen peroxide as oxidant and the dopants phosphoric acid, DBSA and Stearic acid. For the other group was used benzoyl peroxide as oxidant agent and the same dopants phosphoric acid, DBSA and Stearic acid.

Figure 1 shows the SEM micrographs of the lead alloy not coated but polished according chemical deposition procedure (Figure 1a and 1b). It is clear that even after careful polishing, the metallic substrate has deep grooves, which is believed to be the site of conductive polymer nucleation. Following are the micrographs of the lead alloy discs covered with the PPy layer chemically deposited with two different oxidizing agents. The morphology of phosphoric acid-doped lead alloy labels, Figure 1c and Figure 1d, exhibits a structure similar to microspherical cauliflower and a more compact, more adherent and homogeneous polymer layer displayed under the three-dimensional cauliflower structure (within circle). This cauliflower structure is related to the intercalation of the disordered polymer chain (Bazzaoui et al., 2002). For samples that had deposition with DBSA as dopant, the morphology shows the presence of microspheres, being more discrete in the sample with hydrogen peroxide oxidizing agent (Figure 1e). The density of the displayed microspheres was much more consistent in the sample (Figure 1f) that had benzoyl peroxide as oxidizing agent, which resulted in a more porous and less homogeneous polymer layer. For samples in the presence of stearic acid (Figure 1g), the morphology shows the presence of scales, slightly smaller, slightly denser and the presence of pores (within circle) is clear when the hydrogen peroxide oxidant agent was used. The size of the scales is considerably larger and they are overlapping in layers reducing the clear presence of pores (circle) in the sample (Figure 1h) when the benzoyl peroxide was the oxidizing agent. The micrographs also showed that the PPy layers deposited with hydrogen peroxide oxidizing agent presented smaller voids between the grains and were more homogeneous than those that had benzoyl peroxide as oxidizing agent. The morphological differences between each layer deposited with different oxidizing agent can be explained by the oxidation that results in the formation of pores and defects along the PPy chain (Naoui et al., 2000).

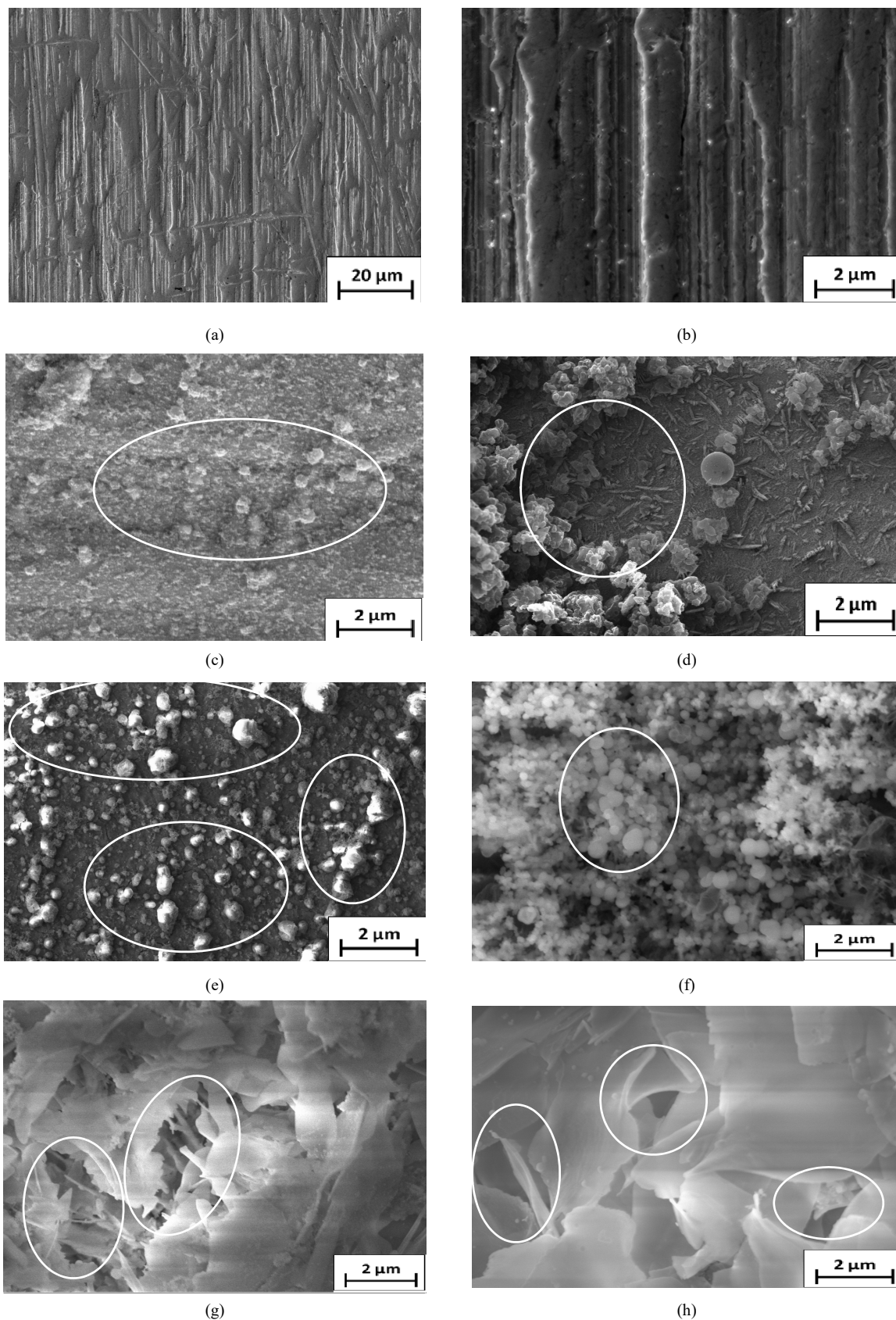


Figure 1. SEM of the lead surface not coated (a) and (b), coated with PPy layer chemically deposited at c) Phosphoric acid + H_2O_2 , d) Phosphoric acid + benzoyl peroxide, e) DBSA + H_2O_2 , f) DBSA + benzoyl peroxide, g) Stearic acid + H_2O_2 and h) Stearic acid + benzoyl peroxide

Each sample that underwent the PPy chemical deposition process had roughness analysis as an important parameter in determining how the formed layer surface will interact with its environment (Bandeira, Drunen, Garcia, & Tremiliosi-Filho, 2017). The results are in Table 2.

Table 2. Roughness analysis results of the layers formed

Oxidizing Agent	Surface	Roughness (μm)
Hydrogen peroxide	lead + PPy + H_3PO_4	0,674
	lead + PPy + DBSA	0,759
	lead + PPy + Stearic acid	8,955
	lead + PPy + H_3PO_4	0,721
Benzoyl peroxide	lead + PPy + DBSA	1,281
	lead + PPy + Stearic acid	1,040

The roughness analysis indicates that the samples treated with both types of oxidizing agent showed different behaviors in the layer formation. For the inorganic dopant (H_3PO_4), the roughness of the layer formed is technically the same, with little difference between the two oxidizing agents, which is shown at the SEM micrography (Figure 1c and 1d). The difference when benzoyl peroxide was used as oxidizing agent with DBSA dopant, show a 70% rougher layer than that when hydrogen peroxide was used (Figure 1e and 1f). For stearic acid, the oxidizing agent that impacted the thickness of the formed layer was hydrogen peroxide, which formed 8.6 times rougher layer than with benzoyl peroxide oxidizer, which is consistent with micrograph showing a porous structure with layers of overlapping scales (Figure 1g and 1h).

3.2 Open Circuit Potential (OCP)

Figures 2 and 3 show the potential versus time curves obtained for the PPy layers of aqueous solutions using hydrogen peroxide (Figure 2) and benzoyl peroxide (Figure 3). The potential of phosphoric acid ranged from -0.35 to -0.39V (Figure 2a) and -0.12 to -0.18V (Figure 3a), presenting a stable behavior in both oxidizing agents. DBSA showed a stable behavior when the oxidizing agent was hydrogen peroxide and remained at a potential around -0.40V (Figure 2b). In the presence of benzoyl peroxide, the initial potential is around -0.02V and drops drastically, oscillating to the end with potential of -0.38V, which is probably due to corrosive processes (Figure 3b). Stearic acid maintained a very stable behavior in the depositions with different oxidizing agents and the potential dropped from -0.07V (Figure 2c) with hydrogen peroxide to -0.45V (Figure 3c) with benzoyl peroxide.

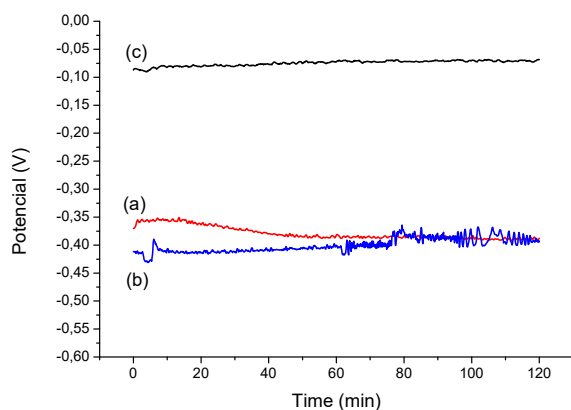


Figure 2. OCP curves for PPy electrodeposition from 0.2 mol.L^{-1} of pyrrole monomer + hydrogen peroxide and different dopants: (a) phosphoric acid, (b) DBSA and (c) stearic acid

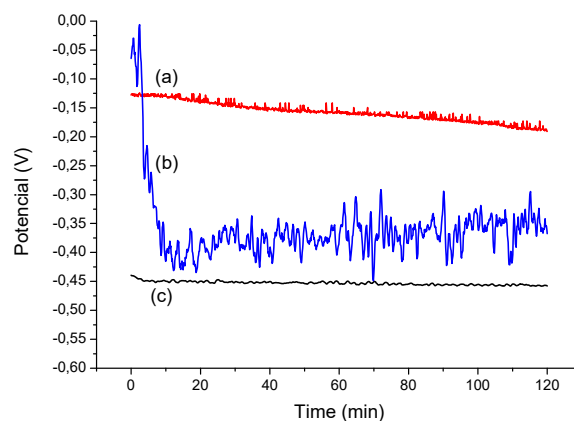


Figure 3. OCP curves for PPy electrodeposition from 0.2 mol.L^{-1} of pyrrole monomer + benzoyl peroxide and different dopants: (a) phosphoric acid, (b) DBSA and (c) stearic acid

Once the lead alloy samples were coated with PPy, they were washed in deionized water and then dipped in 0.1 mol.L^{-1} NaCl corrosive test solution. Lead has relative resistance in HCl, H_2SO_4 and other acids medium, suffers corrosion in HNO_3 and basic medium. Since the interest of this study is to evaluate the behavior of exposed lead in the environment, it was decided to use the medium containing chloride ions. Its potential under open circuit was followed over time relative to the Ag/AgCl reference electrode.

Comparing Figure 2 with Figure 3, the OCP curves showed that the oxidizing agent directly influences the electrochemical response of the formed polymer. The curves have relative chemical stability and generally the most positive displaced potential has an electrochemical system that has a slower corrosive process. It is noteworthy that the results generated by the OCP curves are indicative as to the behavior of the metal in corrosive medium, therefore not being determinant.

3.3 Potentiodynamic Polarization Plots

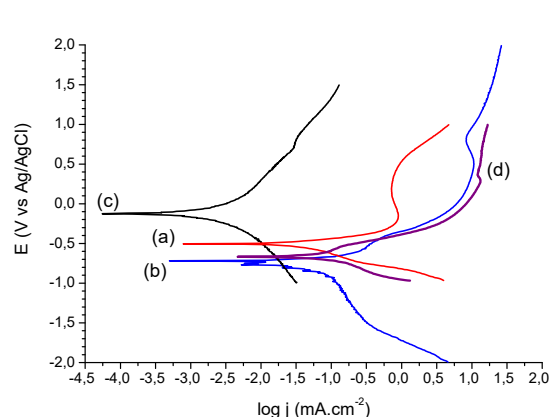


Figure 4. Tafel curves obtained from the polarization plots at 1.0 mV.s^{-1} in aqueous solution 0.1 mol.L^{-1} NaCl for having Hydrogen Peroxide as oxidizing agent: a) PPy + H_3PO_4 b) PPy + stearic acid c) PPy + DBSA d) polished lead alloy surface with no chemical deposition

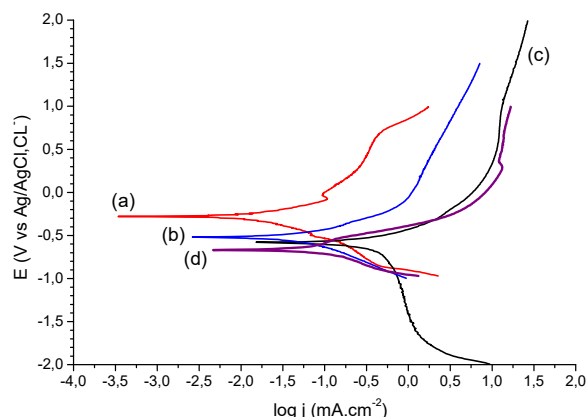


Figure 5. Tafel curves obtained from the polarization plots at 1.0 mV.s^{-1} in aqueous solution 0.1 mol.L^{-1} NaCl for having Benzoyl Peroxide as oxidizing agent: a) PPy + H_3PO_4 b) PPy + Stearic acid c) PPy + DBSA d) polished lead alloy surface with no chemical deposition

Corrosion resistance of lead alloy surfaces coated with PPy films was investigated in medium containing sodium chloride. Figure 4 and Figure 5 show the Tafel curves at 1.0 mV/s in 0.1 mol.L^{-1} NaCl solution. The figures show the curves of the PPy layers chemically deposited with (a) H_3PO_4 , (b) stearic acid, (c) DBSA and (d) uncoated lead alloy surfaces. As shown in the curves, the corrosion potential for coated lead alloy with different dopants has shifted to more positive potentials, than the uncoated lead alloy surfaces, except for curve Figure 4b when the oxidizing agent was hydrogen peroxide.

From the measured corrosion current density, j_{corr} values, the protection efficiency was calculated from the following equation (Yeh et al., 2008):

$$\text{Protection Efficiency (\%)} = \left[\frac{(j_{\text{corr}} - j_{\text{corr PPy}})}{j_{\text{corr}}} \right] \times 100 \quad (3)$$

j_{corr} and $j_{\text{corr PPy}}$ are the corrosion current density values (Table 3) in the absence and presence of the PPy coating with its respective dopants and different oxidizing agents. Extrapolations of the potentiodynamic polarization curves were used to obtain the corrosion current densities (j_{corr}) and thus calculate the corrosion rate. These measurements show that a substantial reduction in j_{corr} occurs for the PPy coated lead. Corrosion protection was significantly more effective when hydrogen peroxide was used as oxidizing agent than benzoyl peroxide, particularly when combined with DBSA. However, it is more effective when benzoyl peroxide was used as oxidizing agent than hydrogen peroxide, particularly when combined with H_3PO_4 .

Table 3. Electrochemical parameters of chemical deposition of PPy with Phosphoric acid, DBSA and Stearic acid as dopants

Samples		$E_{\text{corrosion}}$ (V)	$j_{\text{corrosion}}$ (10^{-4} mA cm $^{-2}$)	% Protection efficiency
Oxidizing agent	Dopant			
Uncoated lead	-	-0,7900	1205,3	-
	H ₃ PO ₄	-0,5088	134,4	88,8
H ₂ O ₂	DBSA	-0,7333	48,1	96,0
	Stearic acid	-4,4135	186,2	84,6
	H ₃ PO ₄	-0,2829	71,3	94,1
Benzoyl peroxide	DBSA	-0,6524	696,4	42,2
	Stearic acid	-0,5797	1093,3	9,27

The effectiveness of corrosion protection of a metallic substrate by an organic inhibitor depends on several factors such as: physicochemical characteristics of the metal substrate, chemical composition of the corrosive medium, chemical structure of the inhibitor (inhibitors containing heteroatoms, triple bonds and aromatic rings) present a higher adsorbent / adsorbate interaction force (Holzle et al., 2005). The presence of organic inhibitors in the reaction medium helps protect against corrosion. Organic inhibitors are molecules that adsorb on the metal surface, reducing the rate of oxidation (anodic inhibitor) or slowing down the reduction reactions (cathodic inhibitor). In comparison, the studies carried out for corrosion protection of aluminum surfaces, it has been observed that surfactants, organic acids andazole derivatives are examples of organic inhibitors (Maayta & Rawashdeh, 2004; Holzle et al., 2005; Branzoi, Golgovici, & Branzoi, 2002; Salghi et al., 2000).

Dopant plays a key role in chemical deposition on metallic surfaces of the conductive polymer PPy. The mechanisms of the deposition process on the surface of the lead alloy consider the formation of a structure containing lead/formed lead oxide/ PPy, and the dopant can influence the formation of pores in the lead oxide layer, which can act as nucleation sites for polymeric film growth. In this study, the dopants used can act as chelating agents forming complexes with lead ions, which can be adsorbed at the oxide / solution interface (Motekaitis & Martell, 1984). Adsorption of the oxide layer may create some difficulty for lead oxidation without inhibiting pyrrole monomer oxidation. However, adsorption of the dopant into the oxide layer may lead to the formation of a very compact layer, thus hindering the pyrrole monomer oxidation reaction, preventing the polymeric layer deposition process. The dope counter-ion, besides influencing the type of lead oxide layer (barrier or porous), is indispensable to balance the charge of the conducting polymers. Both the structure and concentration of the doping ions directly affect the conductivity, morphology and stability of the deposited PPy layers. Dopant concentration and charge density can directly influence ion-ion, chain-chain, ion-chain electrical interactions, thus changing the conductivity of the deposited polymer (Mohammad, 1999). The structure of the dopant may rather affect the solubility of the formed conducting polymer (PPy). Surfactant anions, such as dodecyl benzenesulfonic acid (DBSA), in the polymerization process are incorporated into the polymeric chain where the surfactant diffuses into the spaces between the chains reducing the state of polymer aggregation, favoring the solubility of PPy in organic solvents. Thus, the size of the carbon chain of the dopant influences the conductivity of PPy films and polymerization yield, which decreases with increasing [monomer] / [oxidant] ratio (Song et al., 2004).

4. Conclusion

Pyrrole was successfully polymerized on the lead surface in an alcoholic solution having as oxidizing agent both hydrogen peroxide and benzoyl peroxide combined with each of the proposed dopants (phosphoric acid, DBSA and stearic acid) for the purpose of generate an adherent, homogeneous and effectively corrosion-resistant polypyrrole coating. Early activation of the lead alloy with the oxidizing agent is necessary and allows PPy nucleation to occur *in situ* favoring the formation of the polymer layer. The presence of metal oxide as a passivation layer influences the deposition of the conductive polymer. The structure of the dopant, the size of the carbonic chain of the dopant is determinant in the process of nucleation and formation of the PPy layer and directly influences the conductivity of the formed layer. These polymeric layers associated with dopants show evidence of corrosion protection. However further studies should be done to understand the metal/metal oxide/PPy+dopant interface.

Acknowledgements

To Brazilian National Council for Scientific and Technological Development (CNPq) for the financial support.

Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- Ameer, Q., & Adeloju, S. B. (2005). Polypyrrole-based electronic noses for environment and industrial analysis. *Sensors and Actuators B.*, 106, 541-552.
- Annibaldi, V., Rooney, A. D., & Breslin, C. B. (2012). Corrosion protection of copper using polypyrrole electrosynthesis from a salicylate solution. *Corrosion Science*, 59, 179-185.
- Bandeira, R. M., Drunen, J., Garcia, A. C., & Tremiliosi-Filho, G. (2017). *Influence of the thickness and roughness of polyaniline coatings on corrosion protection of AA7075 aluminum alloy*. São Carlos Chemistry Institute Electrochimica Acta. Elsevier.
- Bazzaoui, M., Martins, L., Bazzaoui, E. A., & Martins, J. I. (2002). New singlestep electrosynthesis process of homogeneous and strongly adherent polypyrrole films on iron electrodes in aqueous medium. *Electrochimica Acta*, 47(18), 2953-2962.
- Branzoi, V., Golgovici, F., & Branzoi, F. (2002). Aluminum corrosion in hydrochloric acid solutions and the effect of some organic inhibitors. *Materials Chemistry and Physics*, 78, 122-131.
- Casas, J. S., & Sordo, J. (2006). *Lead: Chemistry, Analytical Aspects, Environmental Impact and Health Effects*. Universidad de Santiago de Compostela, Spain.
- Diniz, F. B. (2004). *Acumuladores de Chumbo Ácido Automotivos*, 2ª edição.
- Eftekhari, A., & Ahmadi, I. (2006). Electrodeposition of smooth and adherent film of polypyrrole on lead electrode. *Progress in Organic Coating*, 57, 371-375.
- Eslami, M., Speranza, G., Fedel, M., Andersson, N. E., Deflorian, F., Omanovic, S., & Zanella, C. (2019). Electro polymerization and Possible Corrosion Protection effect of polypyrrole coatings on AA 1050 (UNS A91050) in NaCl Solutions. *Corrosion Journal*, 75, 745-755.
- Ferreira, B. R., Liu, A. S., & Cho, L. Y. (2018). Behavior of polypyrrole film chemically polymerized with lauric acid on copper surface. *Material Science Forum (online) JCR*, 930, 434-439.
- Garcia, M. L., & Smit, M. A. (2006). *J. Power Sources*, 158, 397.
- Gurunathan, K., Murugan, A. V., Marimuthu, R., Mulik, U. P., & Amalnerkar, D. P. (1999). *Mat. Chem. Phys.*, 61, 173.
- Holze, R., & Wu, Y. P. (2014). *Electrochim. Acta.*, 122, 93.
- Holzle, L.R.B., Azambuja, D.S., Piatnicki, C.M.S., Englert, G.E. (2005). Corrosion behavior of aluminum in ethylene glycol-water electrolytes containing EDTA. *Materials Chemistry and Physics*, 91, 375-380.
- Lei, Y. H. (2014). *Corrosion Protection of Copper by Conductive Polypyrrole Films Incorporated with Inhibitors* (p. 146). Hokkaido University, Sapporo.
- Liu, A. S., Bezerra, K. M., & Cho, L. Y. (2017). Electrodeposition of polypyrrole on aluminum alloy 2024-T3 from dodecylbenzene sulfonic acid medium. *International Journal of Recent Scientific Research*, 8, 21449-21454.
- Maayta, A. K., & Rawashdeh, N. A. F. (2004). Inhibition of acidic corrosion of pure aluminum by some organic compounds. *Corrosion Science*, 46, 1129-1140.
- Menkuer, M., & Ozkazank, H. (2019). Electrodeposition of polypyrrole on copper surfaces in OXA-DBSA mix electrolyte and their corrosion behavior. *Progress in Organic Coating*, 130, 149-157.
- Mohammad, F. (1999). Comparative studies on diffusion behavior of electrochemically prepared polythiophene and polypyrrole: Effect of ionic size of dopant. *Synthetic Metals*, 99, 149-154.
- Mortazavi, S. H. H., Yeganeh, M., Etemad, A., & Saremi, M. (2019). Corrosion behavior of polypyrrole (PPy) coating modified by polyethylene glycol (PEG) doped ammonium bifluoride on AZ31 magnesium alloy. *Progress in Organic Coating*, 134, 22-32.
- Motekaitis, R. J., & Martell, A. E. (1984). Complexes de aluminum (III) with hydroxy carboxylic acids. *Inorganic Chemistry*, 23, 18-23.

- Naoui, K., Takeda, M., Kanno, H., Sakakura, M., Shimada, A. (2000). Simultaneous electrochemical formation of Al_2O_3 /polypyrrole layers: effect of electrolyte anion on formation process. *Electrochimica Acta*, 45, 3413-3421.
- Pearson, H. A., & Schonfeld, D. J. (2003). Lead. In C. D. Rudolph (Ed.), *Rudolph's Pediatrics* (21st ed.). McGraw-Hill Professional.
- Recycling Economy*. (2017). Beijing University of Technology, Beijing, China.
- Salghi, R., Bazzi, L., Hammouti, B., Bouchart, A., Kertit S., Ait Addi, Z.A., El Alamia, Z. (2000). Étude Electrochimique de l'inhibition de la corrosion de l'alliage d'aluminium 3003 em milieu bicarbonate par les composés triazoliques. *Annales Chimie Science des Matériaux*, 125, 187-200.
- Samad, U. A., Alam, M. A., Sherif, E. M., Alam, M., Shaikh, H., Alharthi, N. H., & Al-Zahrani, S. M. (2019). Synergistic effect of Ag and ZnO nanoparticles on polypyrrole-incorporated epoxy/2pack coatings and their corrosion performances in chloride solutions. *Coatings*, 9, 287.
- Sharifirad, M., Omrani, A., Rostami, A. A., & Khoshroo, M. (2010). Electrodeposition and characterization of polypyrrole films on copper. *Journal of Electroanalytical Chemistry*, 645, 149-158.
- Sheng, N., Lei, Y., Hyonoo, A., Ueda, M., & Ohtsuka, T. (2014). Improvement of polypyrrole films for corrosion protection of zinc-coated AZ91D alloy. *Progress in Organic Coating*, 77, 1724-1734.
- Song, M.K., Kim, Y.T., Kim, B.S., Kim, J., Char, K., Rhee, H.W. (2004). Synthesis and characterization of soluble polypyrrole doped with alkylbenzenesulfonic acids. *Synthetic Metals*, 141, 315-319.
- Sousa, M. C., Lima, J. F., & Vilar, E. O. (2016). *Avaliação da taxa de corrosão em placas de chumbo de baterias automotivas*. I CONAPESC.
- Souza, A. F., Liu, A. S., & Cho, L. Y. (2018). Corrosion protection of 1020 steel by conducting films electrodeposited in methane sulfonic acid. *Journal of Experimental Techniques and Instrumentation*, 1, 41-48.
- Tallman, D. E., Spinks, G., Dominis, A., Wallace, G. G. (2002). Electroactive conducting polymers for corrosion control. *Journal Solid State Electrochemistry*, 6, 73-84.
- Thornton, I.; Rautiu, R.; Brush, S.M. Lead industry profile. In: __. *Lead the facts*. London: Ian Allan Printing, 2001. Available at: <https://www.ilalead.org/UserFiles/File/factbook/chapter4.pdf>
- Vera, R., Schrebler, R., Grez, P., & Romero, H. (2014). The corrosion-inhibiting effect of polypyrrole films doped with p-toluene-sulfonate, benzene-sulfonate or dodecyl-sulfate anions, as coating on stainless steel in NaCl aqueous solutions. *Progress in Organic Coating*, 77, 853-858.
- Xiao, X. K. (2012). Development of American secondary lead industry. *Enterp Technol Dev*, 12, 18-20.
- Yang, J., Hu, C., Wang, H., Yang, K., Liu, J. B., & Yan, H. (2017). Review on the research of failure modes and mechanism for lead-acid batteries. *International J. Energy Research*, 41, 336.
- Yeh, J.M., Yao, C.T., Hsieh, C.F., Lin, L.H., Chen, P.L., Wu, J.C., Yang, H.C., Wu C.P. (2008). Preparation, characterization and electrochemical corrosion studies on environmentally friendly waterborne polyurethane/ Na^+ -MMT clay nanocomposite coatings. *European Polymer Journal*, 44, 3046-3056.

Copyrights

Copyright for this article is retained by the author(s), with first publication rights granted to the journal.

This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).