

Electrochemical behaviors of negative and positive plates lead-acid battery in the presence of polyaniline hydro-soluble in 0.5 M H₂SO₄ medium

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ABSTRACT

The effect of polyaniline hydro-soluble on the current collector in lead-acid battery is performed in order to improve the life of the battery and to protect the collector against corrosion. The polyaniline used in this study is commercial. The electrochemical behavior of the current collectors in the absence and in the presence of PANI hydro-soluble is evaluated by electrochemical techniques: Cyclic Voltammetry, Electrochemical Impedance Spectroscopy (EIS) and polarization curves (Tafel plots) recorded in 0.5 M H₂SO₄ aqueous solution. Long-term cycling is performed by cyclic voltammetry in 0.5 M H₂SO₄ medium. From the results, it's found that the use of polyaniline hydro-soluble in 0.5M H₂SO₄ protects the lead metal within good anticorrosion proprieties. The peaks matching to the oxidation of lead to lead sulfate obtained by voltammetry is decreased for the lead electrode in the presence of polyaniline hydro-soluble compared to the lead electrode without PANI hydro-soluble in acidic solution.

Key-words: -Lead acid-battery, polyaniline hydro-soluble, corrosion, electrochemical techniques.

1. Introduction

For several decades many efforts are made to prevent the corrosion of current collector of lead-acid batteries [1]. The corrosion resistance is a major factor in the development of grids for batteries because it directly affects the performance of the electrochemical cells. Approaches are investigated to minimize the corrosion of lead including the development of more efficient alloys, improved techniques such as electroforming, addition of corrosion inhibitors into the electrolyte or covering the metal with a conductive ceramic as barium plumbate (BaPbO₃) [2,3] or with a conducting polymer thin layers [4,5]. As reported in the literature, very few studies are found regarding the use of conducting polymers such as polyaniline in lead-acid batteries which is aimed by the use of polyaniline as protective coating against grid corrosion and PbO₂ dissolution [6-9]. Moreover, the presence of PANI in H₂SO₄ 0.5 M solution can significantly reduce the corrosion of current collectors when is added to the acidic solution and thereby increases the specific energy density of the battery [10].

In the present work, hydro-soluble polyaniline in 0.5 H₂SO₄ is carefully investigated and its role in the formation of the passive layer is elucidated too. Corrosion studies revealed the efficiency of this polymer in acidic solution for the protection of the current collector of the positive and the negative electrode in lead-acid battery.

2. Methods and materials

2.1. Materials

Lead alloys electrode is used as working electrodes with a grill composition is detailed in Table 1. Working electrode is embedded in an epoxy resin to have a flat exposed area of 1.2 cm²; polished mechanically under water with rough paper from 600 to 1200 mesh and cleaned with special solution (99% CH₃COOH and 1% H₂O₂) before introducing in the electrolyte solution. 0.5 M H₂SO₄ or 0.5 M H₂SO₄/ 0.2 g PANI is used as electrolyte emeraldine form. The conductivity of PANI hydro-soluble is 0.1- 1 S/cm, the density equal to 1.1-1.2 in 20 °C and the dry extract is about 21 wt %.

2.2. Instrumentals and electrochemical tests

The electrochemical performance of the electrode in 0.5 M H₂SO₄ with and without polyaniline is studied at room temperature using potentiostat/galvanostat, AUTOLAB PGSTAT302N. For all experiments, conventional three electrodes cell is used: Lead alloy as working electrode, a platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode.

To study the formation of a passive layer during the immersion of the electrode in sulfuric acid medium supplied by the mechanism of absorption of polymer on the metal surface, such electrode is cycled using voltammetry cyclic in 0.5 M H₂SO₄ with a scan rate of 5 mV/s between the hydrogen and oxygen evolution, in order to confirm the effect of polyaniline on oxidation and reduction peaks on the electrode.

Long-term cycling is performed by cyclic voltammetry in 0.5 M H₂SO₄ medium with a scan rate of 50 mV/s.

In order to evaluate the electrochemical corrosion behavior of the lead alloy electrode, Tafel measurements were also carried out in selected solutions at 25°C. In order to get Tafel plots, all tests are performed by stepping the potential at a scan rate of 0.5 mV/s in the cathodic to anodic direction between ± 300 mV/OCP. Using an automatic data acquisition system. The potentiodynamic polarization curves are plotted and corrosion parameters are estimated by Tafel plots using anodic and cathodic branches.

Electrochemical impedance spectroscopy (EIS) tests are carried out in the same solution with and without polyaniline at 25 °C. Electrochemical impedance spectroscopy (EIS) measurements began after an initial delay of 30 min for the samples to reach a steady-state condition. The sinusoidal excitation voltage applied to the cell is equal to 10 mV with 5 points per decade and the frequency range between 100 KHz to 10⁻² Hz at the open circuit potential is applied.

TABLE 1
Composition of studied Pb alloy

Element	Composition %
Sb	1.90
Sn	0.072
Se	0.022
As	0.097
Ag	0.0015
Bi	0.013
Cu	0.014
Fe	0.0038
Zn	0.0003
Cd	0.0001
Pb	97.87

RESULTS AND DISCUSSION

2.2.1. Cyclic voltammetry

To study the effect of PANI hydro-soluble on the PbSO₄ layer characteristics formed on the lead electrode surface, the CVs of lead alloy electrode in a 0.5 M H₂SO₄ acidic solution with and without PANI, is obtained, as shown in figure 1.

In the anodic potential sweep of the voltammogram, current peak A1 at -0.46 V and -0.316 V/SCE, with and without PANI respectively corresponding to the conversion of lead to lead corrosion products such PbSO₄ (Fig.1) the reduction peak at -0.636 V without PANI and at -0.731 V /SCE within PANI

assigned to the reduction of small and large PbSO₄ crystals (Peak A2, Fig 1) [11]. The intensity of the cathodic peak A7 (transition of PbO to Pb) [11] increases within PANI. The peak A4 [11] indicates the increase of the oxygen evolution and the oxidation of Pb (II) to Pb (IV) as a competitive processus with the oxygen evolution [12]. The transition of α and β -PbO₂ to PbSO₄ (peak A6, Fig.1) increases in the presence of PANI in the solution. The oxidation peaks A3, A'3[12] are related to the oxidation and reduction of antimony and its species respectively [13].

As indicated from current peak A1 in Fig 1, within PANI, the PbSO₄ layer was formed on the electrode, and consequently, the height of the reduction peak of PbSO₄ (peak A2) is increases. Reveal that formed PbSO₄ layer on

the electrode surface are smaller in size and the conductivity of the electrode increases in the presence of PANI in the electrolyte.

A decrease in the height of current peak A7 which is related to transition of PbO to Pb, demonstrates that lower PbO is formed underneath the lead sulfate membrane. Indeed, a decrease in the amount of formed PbSO₄ on the electrode surface prevents from increasing pH underneath the lead sulfate membrane, and consequently, fewer PbO is formed. In the other hand, the increase of current peaks A4 and A6 related to the formation of PbSO₄ from PbO₂ and the reverse reaction. That indicated the increase in the PbSO₄ activity.

In order to confirm the influence of PANI hydro-soluble in the PbSO₄ passive layer and the stability of the film layer, the cyclic voltammogram of the Pb-Sb in the different solutions, is realized. The working electrode is immersed in the polymer solution for half an hour which is the time necessary for obtaining a constant open circuit potential. Fifty cyclic voltammetric sweeps are realized in the PANI/0.5 M H₂SO₄ solution or in 0.5 M H₂SO₄ between -1 and 0.7 V/ SCE.

In 0.5 M sulfuric acid (Fig.2), an anodic peak is observed corresponds to the oxidation from lead to lead sulfate. An increase of the current peak is observed from the first to the 50th sweep. The same behavior is observed for the cathodic peak associated to the reduction of lead sulfate to lead metal (Fig.2). This charge discharge curves (Fig. 2) exhibit reversible characteristics without apparent deviation in each cycle. This suggests the electrochemical stability for the PbSO₄ layer formed in the surface of the electrode. Fig 2 shows the increase of the current peak respectively with the increase of the number of cycle. This result indicates the growth of the PbSO₄ with the increase of the number of cycles.

In the presence of polyaniline in the electrolyte, an abrupt decrease of the current associated to the oxidation of Pb to PbSO₄ (Fig.2) after one cycle is observed. The same phenomena are observed too and this for the cathodic current peaks related to the reduction of PbSO₄ to Pb. The effect can be attributed to the adsorption of organic molecule of PANI on the active sites of Pb. The insulating sulfate layers formed in pure sulfuric acid solution in the current collector increase, so, the Pb-Sb electrode conductivity and the charge discharge properties will be

enhanced. In the presence of the PANI in the acidic solution enhances the stability of the electrode. These results suggest that polyaniline plays the role of corrosion inhibitor in the case of lead in sulfuric acid solution. Indeed, it inhibits lead oxidation and allows the lead sulfate reduction. The polyaniline reduces the corrosion current density of the material.

2.2.2. Anti-corrosion properties of hydro-soluble polyaniline

The corrosion protective efficiency of polyaniline hydro-soluble molecules on lead electrode is investigated by potentiodynamic measurements. From potentiodynamic curve (Fig.4) various corrosion parameters were extracted and are summarized in Table 2. The corrosion current and the corrosion potential are determined by extrapolation of Tafel lines corresponding to the reduction of protons to hydrogen and oxidation associated with the oxidation of lead to lead sulfate. In the presence of PANI hydro-soluble, the corrosion current density decreases and the corrosion potential shifted toward more positive value compared to an as-received lead alloy electrode. Thus, results improve the anti-corrosion properties of lead. This could be due to a decrease of the corrosion defects sites on the metal surface.

2.2.4. Electrochemical impedance spectroscopy

ESI techniques were used to study the corrosion phenomenon.

Fig.3-4. including curves of the imaginary component of the impedance as a function of the real one (Nyquist plots) for the Pb-Sb with and without polyaniline in acidic solution. It can be noted that impedance measurements is carried out after the cycling of the electrode, where the PbSO₄ semipermeable membrane is formed on the electrode surface.

The experimental EIS results (Fig.3-4) reveal that each Nyquist diagram consists of one deformed semicircles.

An equivalent circuit analysis has been conducted. The proposed equivalent circuit used to fit the experimental data is shown in Fig.3a-b. In both figures the calculated values

of the elements of the proposed equivalent circuit obtained by the Zview2 software are shown in table3. In 0.5 M H₂SO₄ the circuit itself comprises one block CPE-R1 connected in parallel to the ohmic resistance R0 of the electrolyte (Fig.3). This entire means that the film formed is considered as a passive layer with a specific resistance R2 of 124.8 Ω/cm². The corrosion layer of PbSO₄, PbO, PbO₂ can affect the performance of the battery. In the presence of PANI into the acidic solution, the equivalent circuit, R1 denotes the electrolyte resistance, R2 is the charge transfer resistance, and R3 stands for a polarization resistance due to the participation of adsorbed intermediates. CPE1-T and CPE2-T denote the double layer capacitance and the capacitance associated with

the polarization resistance R3. The parameters CPE1-P and CPE2-P are correlated with the phase angle, varying between -1 and 1. A constant-phase element representing a shift from an ideal capacitor is used instead of the capacitance itself.

The equivalent circuit elements illustrate that, the resistance of the electrode is increases in the presence of polyaniline into acidic solution. It is in a good agreement with the results obtained by the test of Tafel plot and the results of the cyclic voltammetry. This EIS results confirms the efficiency of PANI hydrosoluble in acidic solution to protect the current collector in lead-acid battery.

Table.2. Results of potentiodynamic polarization test after cycling with and without polyaniline in acidic solution.

Solution	β_c (mV/dec)	β_a mV/dec	E_{corr} (mV/ECS)	I_{corr} ($\mu A/cm^2$)	R_p ($\Omega.cm^2$)	V_{corr} mm/year	Effi %
H ₂ SO ₄ 0.5M	328.37	27.085	-581.58	118.16	91.96	2.93	-
H ₂ SO ₄ 0.5M/PANI (20 cycles cycles)	75.92	213.06	-252.57	935.11 nA	21663	0.027	99.2
H ₂ SO ₄ /PANI (50 cycles)	78.05	124.73	-132.61	3.61	4804	0.107	96.9

Table 3: The equivalent circuit element for Pb alloy in 0.5 M H₂SO₄ or in 0.5 M H₂SO₄/PANI

Solution	Element	Value	Fit Error %
0.5 M H ₂ SO ₄ after 1 cycle	R1 (Ω)	4.27	0.71
	CPE1-T (F)	$8.13 \cdot 10^{-5}$	2.94
	CPE1-P	0.92	0.44
	R2 (Ω)	124.8	0.85
H ₂ SO ₄ 0.5 M/PANI after 1 cycle	R1 (Ω)	3.15	1.19
	CPE1-T (F)	$8.54 \cdot 10^{-5}$	5.36
	CPE1P	0.90	0.71
	R2 (Ω)	113.4	9.39
	CPE1-T (F)	$2.5 \cdot 10^{-3}$	11.56
	CPE1-P	0.48	8.98
	R2 (Ω)	163	9.15

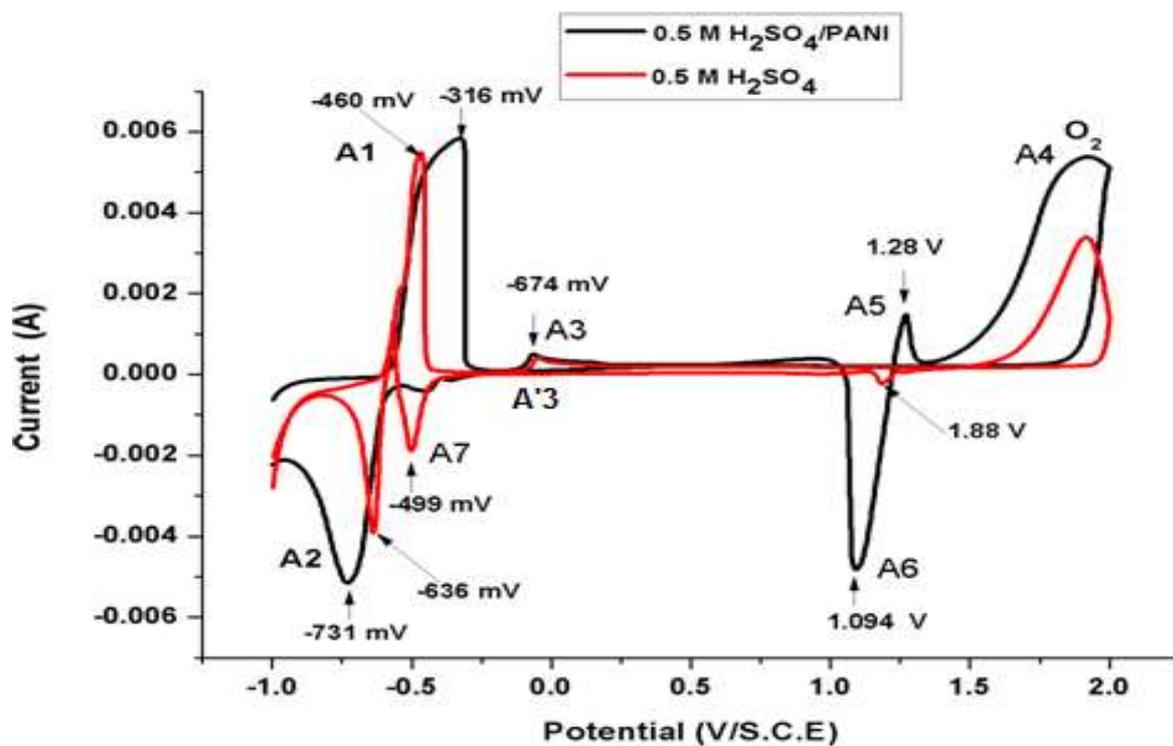


Figure 1 Cyclic voltammograms for a lead alloy electrode in H_2SO_4 with and without PANI solution. Scan rate is 5 mV/s.

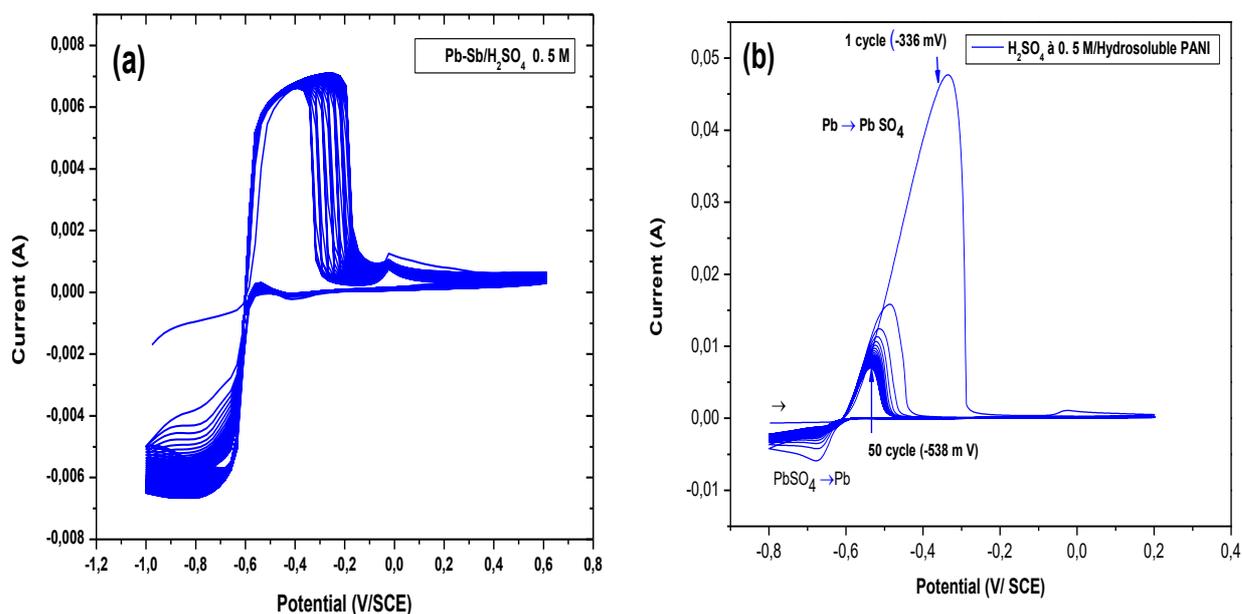


Figure 2 Cyclic voltammograms for lead alloy electrode in H_2SO_4 (a) without and within PANI solution (b). Scan rate is 50 mV/s

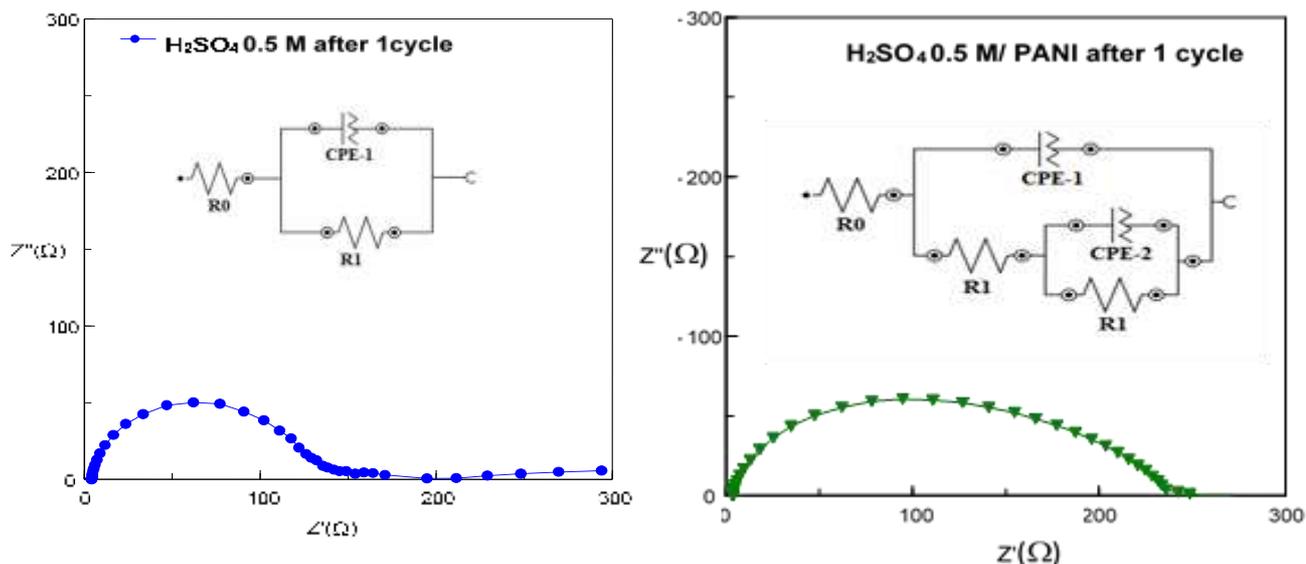


Figure 3
 Nyquist diagram for Pb-Sb: a) in 0.5 M H₂SO₄, b) in PANI/0.5M H₂SO₄ after 20 cycles.

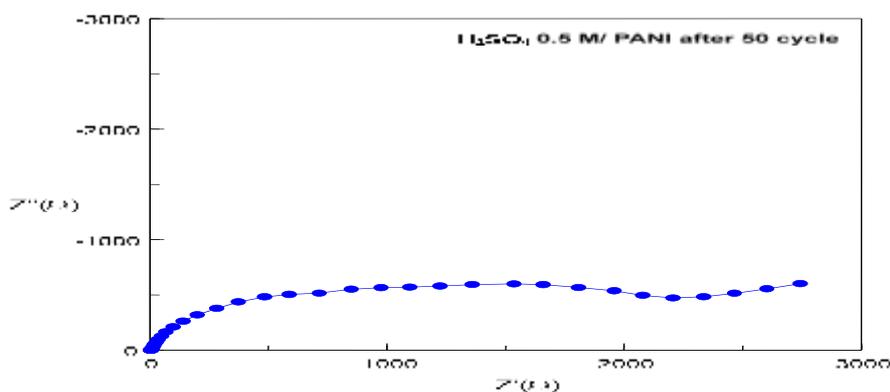


Figure 4
 Nyquist and Bode plots for Pb alloy in the presence of 0.5 M H₂SO₄ / PANI after 50 cycles

3. Conclusion

In this work, it's found that the presence of PANI hydro-soluble in 0.5 M H₂SO₄, reduces the corrosion current density of the Pb-Sb electrode and the resistance of the lead alloy increases at the optimal amount of 0.2 g of PANI. Pb alloy showed a good corrosion resistance in PANI solution.

Through this study of the corrosion behavior of lead alloy, the possibility to use a water-soluble polyaniline in H₂SO₄ acidic electrolyte to protect current collector for the positive electrodes in lead-acid battery, is evidenced.

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