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Effect of Surfactants on the Electrochemical Behavior of the Positive Plate

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The main goal of this research is to improve the performance of positive plate of lead-acid battery using surfactants in 0.5 M H_2SO_4. The use of surfactants aims to increase the ability and the cycle life of the positive active material. The electrochemical behavior of pure lead and PbO_2 electrodes interface was investigated at room temperature by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and potential-dynamic polarization curves. Scanning electron microscopy (SEM) was used to explore the film layer morphology deposited on the surface of working electrodes. Cyclic voltammograms of pure lead (Pb) electrode show that in the presence of PS the current peaks of the transition of PbO_2 to $PbSO_4$ and PbO_2 to $PbSO_4$ dropped at small concentrations of surfactants. We observed a remarkable improvement of the discharge capacity of the PAM for an amount of PS ranging between 10 and 50 ppm. EIS results indicate the improvement of mass transport by the decrease of resistance.

In the other hand, the $PbSO_4$ surface layers and the crystal size of $PbSO_4$ changes with impact effect of surfactants. As a result of the morphological changes which occurred, the PbO_2 films formed are hardly more reducible with $PbSO_4$ and delays the appearance of resistive $PbSO_4$ layers at the material interface. As a conclusion, we can say that the electrical performance of the battery increase by extending the life cycle.

Keywords: lead-acid battery, Surfactant, positive plate, Electrochemical Impedance Spectroscopy (EIS), SEM, and Electrochemical Techniques.

1. INTRODUCTION

One of the most important batteries used in Algeria is lead-acid battery, composed by lead dioxide (PbO_2) and spongy lead (Pb) as the positive and the negative active material respectively. The performance of these batteries was affected by the structural properties of the active material. Their advantages are mainly their low initial cost, high safety, easy construction and low self-discharge compared to other sophisticated batteries, however, exception for the polluting nature of Pb and its compounds [1].

During the production of lead-acid batteries, the plates remain in H_2SO_4 solution for a certain period at open circuit potential. PbO and 3BS are unstable and react chemically with H_2SO_4 whereby the paste is sulfated. The process during Soaking of 3BS and 4BS plates has been investigated by several authors [2-7]. It has been established that the sulfation of the plates is mainly influenced by the phase composition of the cured plate, H_2SO_4 concentration and soaking time. The industry of lead-acid battery in Algeria is currently suffering from this problem (visit on site).

The polarization of Pb in sulfuric acid leads to a number of reactions mostly (1) and (2) [8-9].

$$Pb + SO_4^{2-} \longleftrightarrow PbSO_4 + 2\,e \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$PbO_2 + SO_4^{2-} + 4\,H^+ + 2e \longleftrightarrow PbSO_4 + 2H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The formation of hard sulfate occurred, when rechargeable lead sulfate crystals were produced during the discharge process. At the initial stage, the sulfate crystal initially formed under discharge cycle was up to 1 µm in diameter. After 8 days, it grew to 5 µm and reached up to10 µm after 5 months of use. The $PbSO_4$ scales grew on the positive and the negative electrodes [10].

It was observed a passivation layer of lead in the sulfuric acid solution composed by insoluble $PbSO_4$ on the specimen surface. Many workers showed the performance limitation of the positive plate compared to the negative one, the reason why additives were used to increase its capacity [11-14].

Increasing the pH electrolyte within the $PbSO_4$ layer conduct to the appearance of PbO and basic lead sulfates (3BS, 3BS) under it and consequently passives the electrode [15, 16].

Some workers showed that additives in the electrolyte can improve the performance of lead battery [17-23] understanding that they must be stable in corrosive electrolytes [18].

In this research investigation, positive plate were studied in terms of the electrochemical behavior in sulfuric acid solutions both in the absence and in the presence of two surfactants that are a mixture of Alkyl phosphonate (20-40%), Polykarboksylsyre Copolymer (10-20%) (PSN°1) and Organic ammonium phosphonates (10-30%) (PSN°2). The main purpose of this work was to elucidate the influence of the formed PbO_2 and $PbSO_4$ layer of various concentration of an electrolyte PS addition. We noticed that as we add surfactants in small concentrations we obtain a considerable performance improvement of the lead-acid batteries.

2. EXPERIMENTAL

2.1. Material and reagents

All solutions were prepared by using analytical reagent grade; pure lead and positive plates were supplied by the Unit of Accumulators located at Oued Smar city at the Algerian capital’s suburb.

The studied media was 0.5 M sulfuric acid containing PS in the concentration of (0, 5, 10, 15, 20, 30, 50,100, 200 ppm).

2.2. Apparatus

Electrochemical necessary technical were conducted by a potentiostat/galvanostat AUTOLAB PGSTAT302N using a conventional three-electrode system. A working electrode (positive plate or pure lead (Pb)), the counter electrode was a rod Platinum, and the reference electrode was a saturated calomel electrode (SCE) as reference electrode and carried out at a temperature of 25 ± 1 °C. All potential values are reported in V versus SCE.

The working electrodes consisted of a conductor wire soldered with a coupon of 8.5 cm^2 for the positive plate and 2.16 cm^2 around the pure lead. The isolation was obtained with an epoxy resin. The positives plates were made according to the "Flat Plate" technology. The active material PbO_2 was made from sulfuric acid and a powder consisting of a mixture of lead oxide powder, metallic lead and paraffin oil. The grids consisted of antimony alloy and lead of secondary fusion. The grids were supplied by the Unit of Accumulators Setif-Algeria.

Before each measurement, Pb surfaces were polishing mechanically under water with emery paper from 600 to 1200 mesh, then degreased in alcohol and rinsed with distilled water. In order to reduce the oxides formed in the surface by contact with air, the electrode was polarized for 10 minutes at -1 V before each experiment.

2.3. Electrochemical measurements

To study the effect of PS on the characteristics of the electrode surface, cyclic voltammetry (CV) were conducted at a sweep rate of 5 mV s^{-1} in the potential region (0.4 to +2 V vs. SCE).

Microstructure of the positive electrode plates were obtained with SEM images. Similarly, the effect of the PS's behaviour on the corrosion of working electrodes was evaluated by using the Tafel plot technique (from –250 to 250 mV/E_{corr}) at the scan rate of 0.1 mV s^{-1}.The electrochemical impedance spectroscopy (EIS) measurements of the positives plates were performed in the frequencies region from 10^5 Hz to 10^{-2}Hz, with AC voltage amplitude of 10 mV.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

Electrochemical behavior of pure Pb or lead alloy in the anodic and cathodic regions have already been cited in details [24- 30]. In our recent experiments lead alloy electrode was studied in 0.5 M H_2SO_4, the results indicate that the peaks current related to oxidation of Pb to Pb^{2+} ($PbSO_4$ formation), the reduction of $PbSO_4$ to Pb and the transition of PbO to Pb were decreased in the presence of PS studied [31].

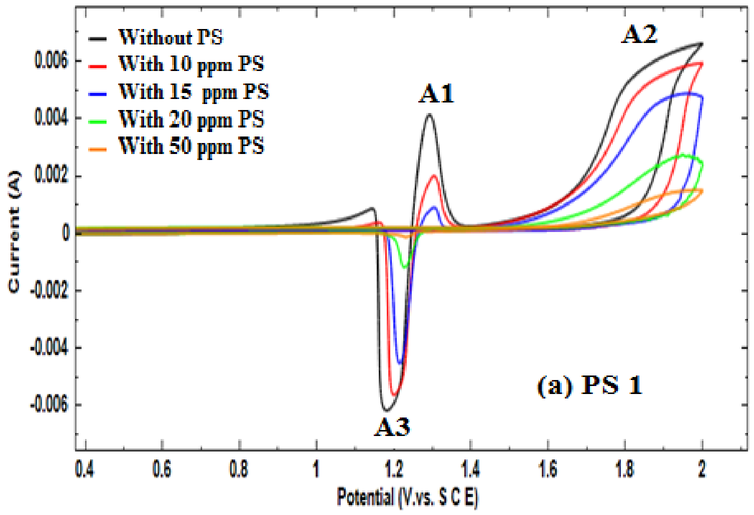
In this paper, we extend our investigations by studying the positive plate and the pure lead (Pb) rather than lead alloy electrode. We will discuss the portion of the dioxide PbO_2 obtained during oxidation and subsequent reduction processes. Cyclic voltammograms of pure Pb electrode, obtained within the potential range of 0.4 to 2 V/SCE in 0.5 M H_2SO_4 at a scan rate of 5 mV s^{-1} in the presence of various concentrations of PS and without PS, are presented in Fig.1.

The voltamogramm obtained for sulphuric acid solution (without PS) show the presence of two peaks A1 and A3 corresponding to the PbO_2 formation [32, 33] and α-PbO_2, β-PbO_2, to $PbSO_4$ [34, 35] respectively.

In the presence of a successive addition of PS N°1 (10, 15, 20 ppm) in 0.5 M sulphuric solution, the voltammograms show that the peak currents corresponding to A1 and A3 are decreased with increasing the concentration of PS N°1. In the presence of 50 ppm of PS N° 1, the peak A1 and A3 were disappeared. In the other hand, the presence of PS N° 2 leads to the disappearance of the peak A1 and A3 beginning from 10 ppm. The peaks potential and the peaks current values were summarized in Table I.

Table I. Cyclic voltammetry results for pure Pb in 0.5 sulphuric acid with and without the addition of PS N° 1 and PS N° 2.

Concentrations of PS	PbO_2 formation (peak A1)		$PbO_2 \rightarrow PbSO_4$ (peak A3)		Oxygen evolution (peak A2)	
	E (V)	I (A)	E (V)	I (A)	E (V)	I (A)
Without PS	1.30	3.8 . 10^{-3}	1.18	-6.1 . 10^{-3}	1.98	6.4 . 10^{-3}
With 10 ppm PS 1	1.30	1.79 . 10^{-3}	1.20	-5.5 . 10^{-3}	1.97	5.9 . 10^{-3}
With 15 ppm PS 1	1.31	0.8 . 10^{-3}	1.21	-4.4 . 10^{-3}	1.96	4.9 . 10^{-3}
With 20 ppm PS 1	-	-	1.22	-1.1 . 10^{-3}	1.96	2.7 .10^{-3}
With 50 ppm PS 1	-	-	1.23	-8.42 . 10^{-5}	1.95	1.5 .10^{-3}
With 10 ppm PS 2	-	-	-	-	1.97	0.7 . 10^{-3}
With 15 ppm PS 2	-	-	-	-	1.97	0.7. 10^{-3}
With 20 ppm PS 2	-	-	-	-	1.96	0.1. 10^{-3}
With 50 ppm PS 2	-	-	-	-	1.95	0.1. 10^{-3}



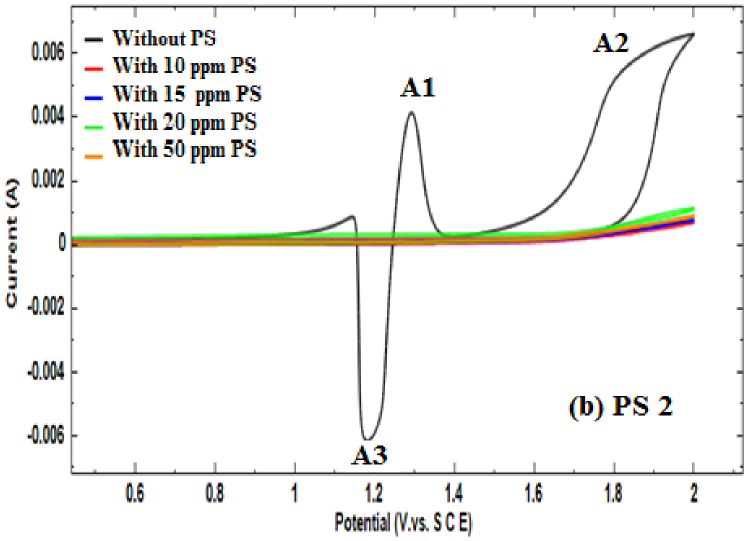
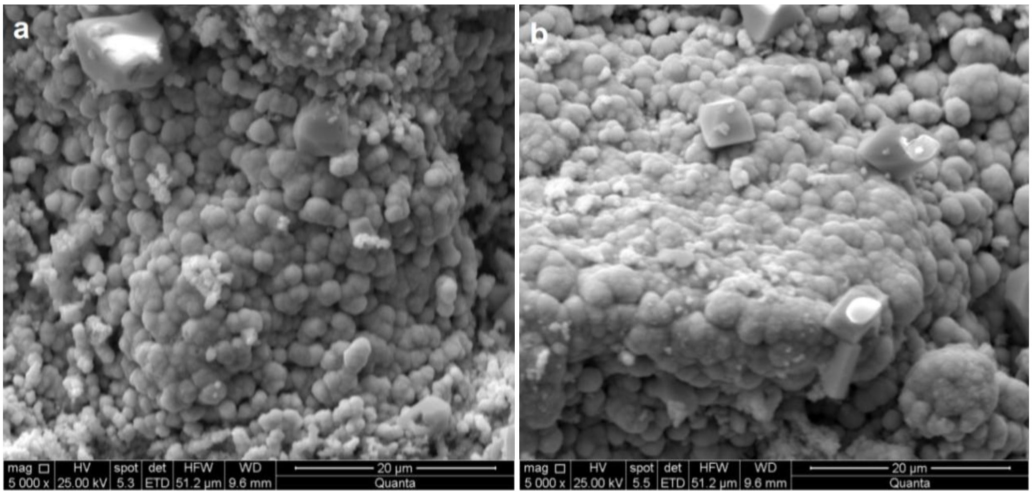


Figure 1. Cyclic voltammograms portion of pure Pb electrode in 0.5 M H_2SO_4: (a) In the presence of PS N° 1; (b) in the presence of PS N° 2, at a scan rate 5 mVs^{-1}.

The addition of PS decrease or inhibits the formation of PbO_2, this indicates that the presence of PS in acidic solution retard the reduction reaction, i.e., the discharge capacity of the positive plate is decreased.

Another notable aspect on the anodic scan is the oxygen evolution. The results of the voltamograms in Fig. 1 indicate that in the presence of the two studied PS, the oxygen evolution potential shifts slightly to the positive direction with decreasing current peak (Table I). This is an indication of the performance of the positive electrode [36]. The peak related to the transition of α and β- PbO_2 to the $PbSO_4$ (A2) were dropped in the presence of the PS studied. PS have decreased the oxygen evolution and the conversion of $PbSO_4$ to PbO_2 (Fig. 1).

The SEM images (Fig.2) shows the presence of a minor quantity of $PbSO_4$ on the electrode surface when the solutions were treated with PS N°1 and PS N° 2. These molecules inhibit the formation of lead sulfate on the surface of the electrode. The presence of PS in solutions reduces the crystalline formation of $PbSO_4$. PS's act as film and prevent the attraction between Pb^{2+} and SO_4^{2-}.



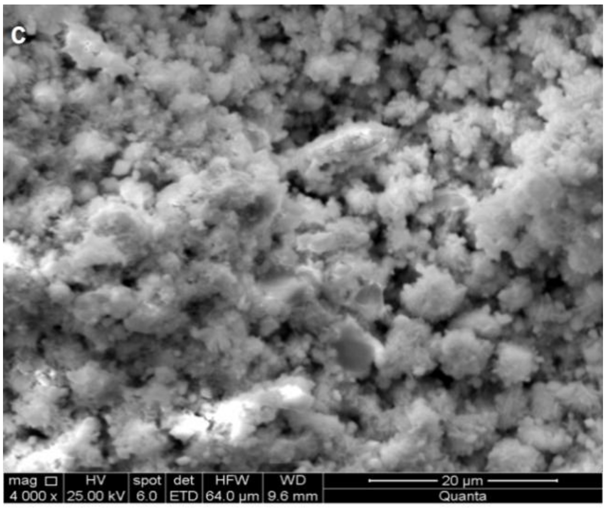
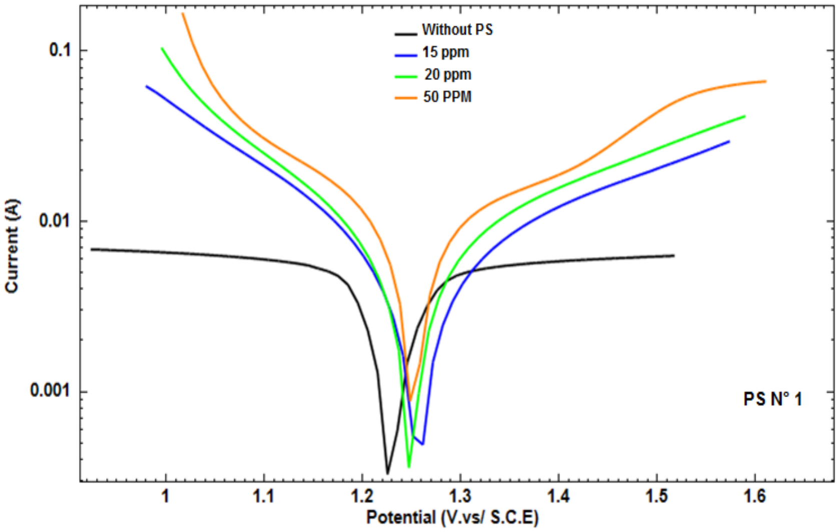


Figure 2. SEM imaging of PbO_2 after one cycle of charge/discharge in H_2SO_4: (a) without PS, (b) with the presence of PS N°1 and (c) with the presence of PS N° 2.

3.2. Potentiodynamic curves

The results obtained from the Tafel plots (Fig.3) are summarized in table II.

The electrochemical parameters given in table II indicate that the current recorded at the potential of 1.35 V that correspond to the active regions located at $E_{(i = 0)}$ = +7mV.This anodic currents (i_a) given in table I taken at potential of E= 1.35 V make a comprehensive comparison between the acidic solution with and without PS. As revealed in Fig.4, the current in the anodic branch increase with the addition concentration of PS. In the absence of PS, the anodic branches (Fig.1) show a plateau of passivation caused by the growth of a barrier of $PbSO_4$ layer on the electrode surface (positive plate). The addition of PS reduces the effect of this barrier and the anodic curves of Tafel plot (Fig.3) became active. The shape of the Tafel plots is the same for all concentrations in the two solutions with PS's.



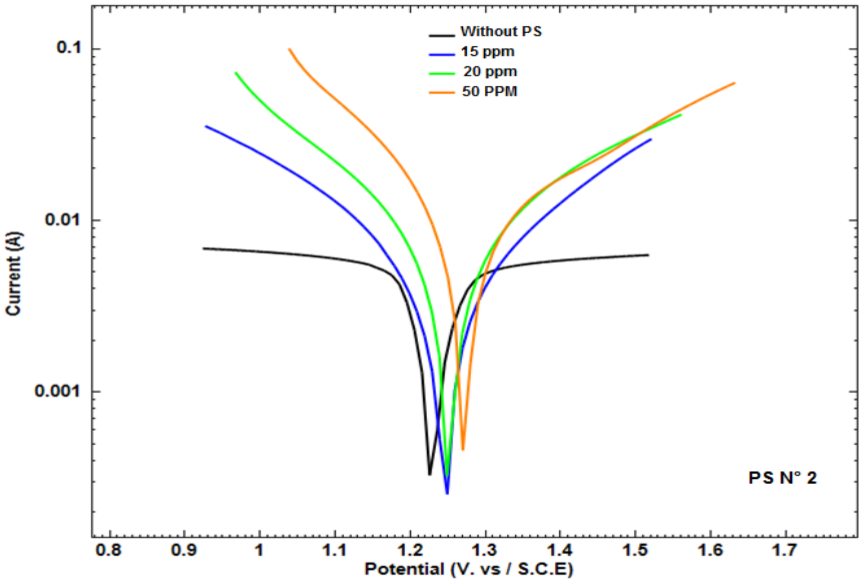


Figure 3. Experimental potentiodynamic polarization curves of the positive plate, in the absence and in the presence of PS N°1 and in the presence of PS N°2

Table II. Electrochemical parameters data from Tafel plot for positive plate in sulfuric solution with and without PS N°1 and PSN°2

Surfactants	Concentration of PS (ppm)	$E_{i=0}$ (V. vs.E.C.S)	i_{Corr}(mA/cm^2) at $E_{i=0}$	i_a(mA/cm^2) at E = 1.35 V
Without PS	00	1.228	8.07	0.65
PS N° 1	15	1.245	0.931	1.20
	20	1.251	1.389	1.23
	50	1.271	1.571	1.57
PS N°2	15	1.251	0.989	1.01
	20	1.253	0.743	1.47
	50	1.255	0.601	1.80

With the addition of PS, at the equilibrium potential $E_{i=0}$, the curves indicate the enhancement of the passivation properties of the layer formed by crystals of $PbSO_4$ on the surface of the electrode. With the presence of PS Tafel plots show a slightly shift toward the positive values (Fig.3). These curves signify the role of PS in the decrease of the formation of $PbSO_4$ layer. The current values in the active region, not far from the equilibrium potential were high and increase with the concentration of PS (table II). It is assumed that the presence of PS in the solution of H_2SO_4 inhibits the formation and the growth of the film of $PbSO_4$ and/or the film of the $PbSO_4$ became more porous.

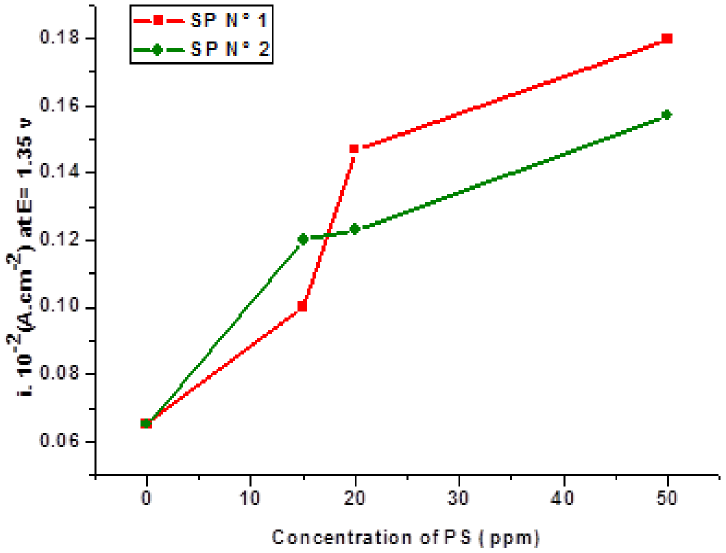


Figure 4. Anodic current density at E = 1.35 V of the positive plate with and without PS at different concentration in 0.5 M H_2SO_4

3.3. Electrochemical impedance spectroscopy (EIS)

The EIS measurements were carried out at the open circuit potential (1.28 Vvs S.C.E). The ions sulfates were adsorbed at the PbO_2 surface and form $PbSO_4$ layer limiting ions mobility between the solution and the active surface.

Fig.5 shows curves of the Nyquist spectrum of the positive plate electrode recorded at the equilibrium potential and the bode representation of the same diagrams are shown in Fig. 6 that indicate the presence of one constant time. The EIS results picked from Nyquist diagrams is shown in table III. Each impedance diagram consists of one semicircle slightly flattened.

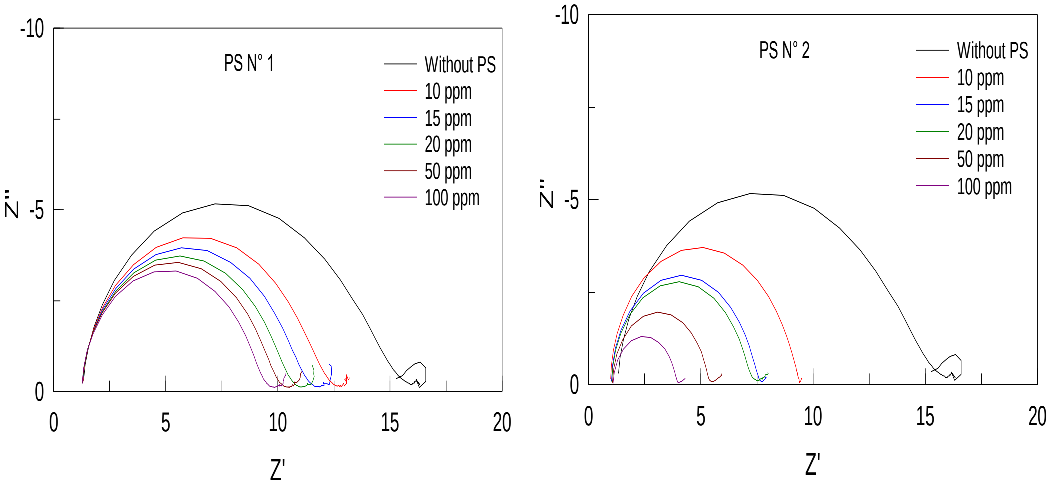


Figure 5. Experimental Nyquist of PbO_2 working electrode with and without PS at different concentration in 0.5 M H_2SO_4

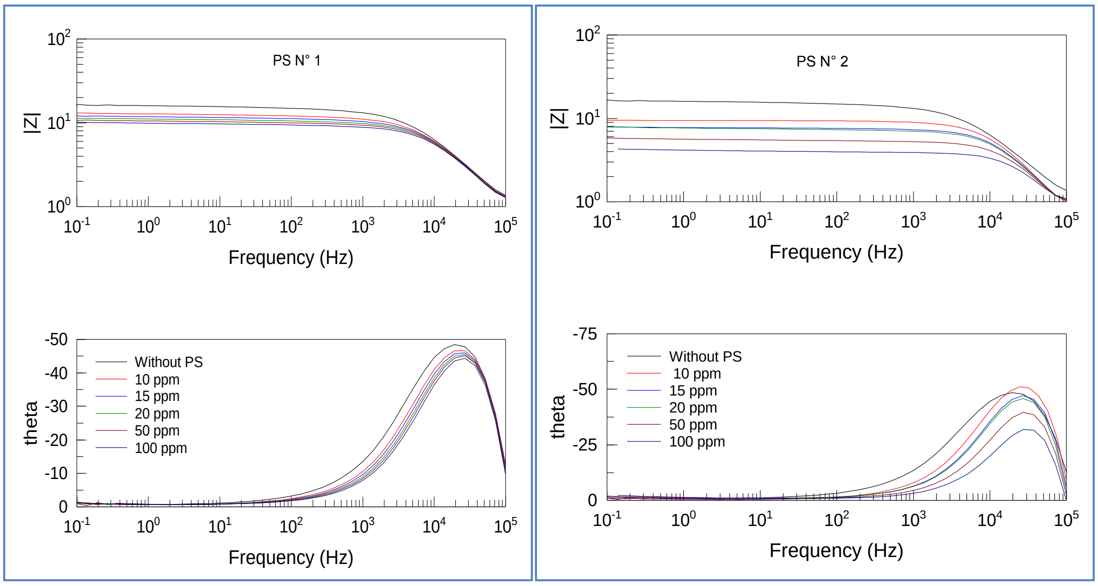


Figure 6. Experimental Bode diagrams of PbO_2 working electrode with and without PS at different concentration in 0.5 M H_2SO_4

The spectrum recorded in the absence of PS shows at low frequencies an inductive loop that characterizes the relaxation phenomena due to the adsorbed species of $PbSO_4$ that form barrier on the surface of working electrode (positive plate). The resistance of polarization is higher without PS. The addition of PS affects the growth of $PbSO_4$ crystal and decreases these resistances (table III).

The equivalent circuit simulating the interface electrode/solution proposed to describe the impedance behavior of the positive plate in 0.5 M H_2SO_4 solution at the potential of 1.28V is given in Fig.7.

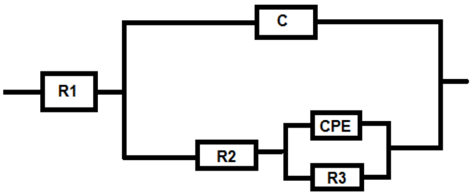


Figure 7. Electrical equivalent circuit of the positive plate electrode in 0.5 M H_2SO_4

The equivalent circuit is formed by R1 (resistance of electrolyte) connected in serial with the capacity (C) of the PbO_2/electrolyte that is connected in parallel with the resistor of polarization (R2) and the block CPE-R3 related to the $PbSO_4$ film. As indicated in the Fig. 5 and the Fig. 6, it's clearly shown the effect of PS on the shape of impedance diagrams. The addition of PS's in the solution renders decreasing in the growth of $PbSO_4$ crystal and the diameter of semi-circles in the absence of PS's were the largest than those recorded in the presence of PS's. With increasing PS concentration, the sulfate layers become more permeable. The CPE element characterizes the non-uniform charge distribution at the $PbSO_4$ film that indicates the presence of a permeable structure of this film.

Table III. Parameters data Of PbO_2 electrodes in 0.5 M H_2SO_4 obtained from EIS diagrams

Surfactants	Concentration of PS (ppm)	R1 (Ω. cm^2)	C1 (μF/cm)	R2 (Ω. cm^2)	CPE.T. (μF/cm)	CPE.P	R3 (Ω. cm^2)
Without PS	0	1.42	2.47	9.65	29.8	0.73	6.33
With PS N°1	10	1.38	2.51	8.26	29.0	0.71	6.14
	15	1.36	2.54	7.75	22.6	0.75	4.58
	20	1.35	2.58	7.36	21.2	0.75	4.39
	50	1.33	2.61	6.89	17.2	0.79	3.11
	100	1.32	2.66	6.51	18.1	0.78	3.11
With PS N°2	10	1.01	2.68	7.26	09.3	0.85	2.23
	15	1.08	2.91	5.83	10.1	0.82	2.34
	20	1.09	3.06	5.47	08.8	0.86	1.42
	50	1.12	3.44	3.88	08.7	0.87	1.06
	100	1.15	4.35	2.58	08.4	0.91	0.44

4. CONCLUSION

Reduction/oxidation peaks of PbO_2 recorded with CV technique are higher in the absence of PS's and they shift down when PS's at different concentrations were added. The current of the oxidation/reduction process is related to the amount of $PbSO_4$ layer that is more important in the absence of PS's. The current in the active region is increased by the addition of surfactants in the solution.

The resistance values in the absence of PS are higher compared to the results obtained with the addition of surfactants.

The surfactant substantially changes the morphology of the deposit of the lead sulfate on the positive plate (PbO_2 electrodes).

The main results of this study indicate that the use of surfactants at a low concentration (5-20 ppm) in the acidic solution of lead acid batteries can increase the capacity of the positive plate of the studied battery and also extend their life cycle.

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