The Effect of Surfactants on the Efficiency of Lead Acid Batteries

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Abstract

The aim of this study is to show the effect of two phosphonate surfactants (PS) on the electrochemical behavior of the negative plate of lead-acid battery in the sulfuric acid medium. The characterization of the electrode interface was investigated at room temperature by a set of electrochemical techniques as linear sweep voltammetry (LSV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA). Scanning electron microscopy (SEM) was employed to determine the film layer’s morphology deposited on the surface of working electrodes, in the presence and in the absence of the PS. When the PS was added in the acidic solution, hydrogen evolution became higher, the over-potential of hydrogen was shifted to negative values and the growth of the anodic $\beta$-PbO\textsubscript{2} was inhibited. SEM imaging with the presence of PS showed reduction in the growth of the anodic $\beta$-PbO\textsubscript{2} and PbSO\textsubscript{4} layers. EIS results indicate the decrease of the conductivity of $\beta$-PbO\textsubscript{2} film on the lead surface electrode. The result of the CV, show a decrease in the peak related to transition of PbO to Pb demonstrates that lower PbO has been formed underneath the lead sulfate membrane in the presence of low concentration of SP indeed a decrease in the amount of formed PbSO\textsubscript{4} on the electrode surface.

1. Introduction

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Keywords: Corrosion; Surfactant; lead-antimony alloy; Electrochemical Impedance Spectroscopy (EIS); SEM, Electrochemical Techniques.
During the last two decades the Lead-acid batteries (LAB) has been widely used in battery driven vehicles and for storing chemical energy (Rezaei et al (2011), M. Fogiel (2003)). Labs offer a number of advantages including low cost of manufacture, easy of charge and good specific power when compared to other advanced batteries (Ponraj et al, 2009, Berghult et al, 1998).

In spite of their rapid performance and design improvements, there remain to solve some LAB internal electrochemical processes. For instance, the grids are usually made of lead-antimony alloys containing 3 to 11 wt % antimony to improve the mechanical properties of the grids (Crompton, 2000). However, antimony decreases over-potential of hydrogen evolution at the negative plate (Hirasawa et al, 2000, Rogatchev et al, 1976). The absence of antimony in the grid of the positive or in the negative electrode of the battery may decrease its capacity during charge-discharge cycling (Bunic et al, 2005). The use of surfactants (SP) in the constitution of the acidic electrolyte can offer an improvement of the battery capacity.

Henceforth, the suitable SP must be chemically, thermally and electrochemically stable within highly corrosive environments. We present in this study a stable SP solution composed of the following additives: mixture of Alkylphosphonate (20-40%) and Polykarboksylsyre Kopolymer (10-20 %)(SPN°1); Organic ammonium phosphonates(SP N°2). We have measured many parameters while we add this stable solution within a range of concentration in the acidic solution of a LAB and we gained many performance improvements in the electrochemical behavior of its individual electrodes.

2. Experimental

The interface electrodes/electrolyte (sulfuric acid0.5M), with and without PS has been performed by: cyclovoltammetric (CV), linear Sweep voltammetric (LSV) and electrochemical impedance spectroscopy (EIS) measurements by using an AUTOLAB PGSTAT 302N monitored by a computer. The electrode potential was referred to the saturated calomel electrode (SCE). A large surface of platinum (Pt) was used as an auxiliary electrode. The working electrode was made in lead alloy-1.97%Sn-Sb (the surface area of the electrode is 1.2 cm²) and the negative plate surface area was 8.5cm². The working electrode (lead antimony) was polished with emery paper (600, 800, 1200 mesh) under water and cleaned with special solution (99% CH₃COOH and 1. %H₂O₂). The working electrode was washed with double-distilled water and ethanol before introducing it in the electrolyte solution.

3. Results and discussions

3.1. Cyclic voltammetry

The CV of lead 1.97 % antimony electrode in 0.5 M H₂SO₄ performed in the potential region between hydrogen and oxygen evolutions (from -1 to 2 V vs. SCE) is shown in the Fig.1. The current peak (a) is corresponding to the formation of lead sulfate (Metikohukovic et al, 1994, Ijomah,1987). The transition from PbO₂ to PbSO₄ (b), and from PbO to Pb (c) occurs during the cathode potential sweep (Sharpe,1975, Mahato et al, 1983, Guo, 1996 and 1992, Caldara et al, 1980). The current peak (d) was assigned to the reduction of small and large PbSO₄ crystals respectively. The oxidation current peak Aₓ at a potential about 0.00 V and the reduction current peak Cₛ at a potential of -0.25 V is related to the oxidation and to the reduction of antimony and its species respectively [9].

The oxidation of antimony begins at the PbO formation potential within a semi permeable layer of PbSO₄. The peak current for both reduction and oxidation decreases with the addition of small amount of SP in cell solution as shown in Fig. 1 (Peak (a) and (d)). The formed PbSO₄ crystal on the electrode surface in the presence of two SP is smaller in shape. The passive layer covering the lead electrode was formed by lead monoxide, underneath the PbSO₄ layer. The decrease in the current peak Aₓ, that is related to transition from PbO to Pb demonstrates that lower PbO has been formed underneath of the lead sulfate layer. With the presence of SP (Fig.1), the potential of oxygen evolution moves toward positives values with a decrease in the current peak.
The presence of SP in the solution may inhibit the oxygen evolution without the formation of β-PbO₂. Fig.1 shows that the effect of two SP have similar effect with the oxidizing current of Pb to PbSO₄ (peak a), also the current corresponding to lead sulfate formation decreases with the addition of SP or by increasing their concentration. The small scale of PbSO₄ was formed on the electrode surface that leads to the increase of the current of the reduction of PbSO₄.

3.2. Hydrogen evolution potential

The hydrogen potential evolution can affect the performance of the lead-acid battery. As shown in Fig. 2, the LSV of Pb-1.97 Sb-Sn alloy in the presence of 10 ppm of SP’s in the 0.5 M sulfuric acid electrolyte, the potential of hydrogen evolution potential shifts towards more negative values.

The addition of SP’s at 10 ppm in the acidic solution was affected the potential of lead electrodes with the increase of hydrogen reduction. The potential was shifted toward the negative values related to the blank sample (Fig. 2a). The evolution of potential versus concentration of SP’s is shown in Fig. 2b obtained at the current density of 3.5 mA.
Fig. 2. Linear weep voltammograms of Pb-1.97 Sb-Sn alloy at a sweep rate of 5 mV/s in 0.5 M sulfuric acid electrolyte without and with SP (SP N° 1 or SP N° 2); a) in presence of 10 ppm of SP b) in the presence of different concentration of SP (5,10,15,20,30,50, 100, 200 ppm).

Hydrogen evolution potential is shown in Fig.2-b. At the lower concentration of SP the hydrogen evolution is decreased. However, at the intermediate concentration, it is noticed the increase of the hydrogen evolution but for the concentration of SP’s between 100 and 200 ppm, the hydrogen evolution was increased.

The morphology of the lead alloy after one cycle of charge/discharge in sulfuric acid solution with and without the SP N°1 and the SP N°2 is shown in Fig.3. The SEM images of the fig.3 confirm the formation of smaller and fewer amounts of PbSO₄ with the presence of SP (Fig 3c).

It seems that SP molecules interact with surface electrodes causing the change in the structure and in the shape of the lead sulfate on the electrode surface. It seems that SP these molecules prevent the contact between lead and sulfates ions to form lead sulfate crystals and the growth of lead sulfate crystals is stopped.

3.3. Electrochemical impedance Spectroscopy (EIS)

The Nyquist plot of impedance of the negative plate electrodes shown in Fig.4 consists of a semicircle and a straight line. The semicircle is related to charge transfer resistance and double layer capacitance formation. It can be observed that the diameter of semicircle that is related to charge transfer resistance is increased with the addition of SP. The impedance spectrums show the increase of the resistance parts of the negative plate with the increase SP concentration. This result is not in accord with the previous results obtained by CV and LSV. This disagreement may be related to the mixture of PbSO₄ and PbO that need further investigations.
4. Conclusion

If we provided the presence of low concentration of PS in the sulfuric acid of lead-acid batteries (LAB) such as a compound solution of two SP (SPN°1, SP N°2), fewer PbSO₄ crystals are formed on the electrode surface. The later are the main cause of morphological changes of the PbSO₄ layer and play an important role in the electrochemical reactions of the lead alloys. Moreover, different crystals structures of PbSO₄ have effects on the hydrogen and oxygen evolution. Indeed, the CV electrode shows that increasing the concentration of SP increases the conversion current of PbSO₄ to PbO₂ while decreasing the reversibility. The adsorption of the molecules of SP on the active sites of PbO₂ layers in the electrolyte at low concentration has a beneficial effect on the charge/discharge characteristics of negative and positive plates and on the cycle life of the LAB. Also, the results show that using the SP in a very low concentration (5-20 ppm) can improve the electrochemical performance of the LAB.

5. References

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