SODIUM LAURYL SULFATE EFFECTS ON ELECTROCHEMICAL BEHAVIOR OF POSITIVE ACTIVE MATERIAL AND COMMERCIAL POSITIVE PLATES IN LEAD-ACID BATTERY

Xuan Thang Nguyen[1, *], Duy Ket Nguyen[1], Thi Hanh Pham[2], Minh Thanh Vu[1]

[1]*Science Institute of Military Technology, 17 Hoang Sam Street, Cau Giay Dist, Ha Noi*

[2]*Center for Research, Consultant and Chemical Technology Transfer, 77th, 337 Ward, Cau Giay Dist, Ha Noi*

[*]Email: *Thangcnhh256@gmail.com*

ABSTRACT

Sodium lauryl sulfate (SLS) is an anionic surfactant used in many applications such as cleaning and hygiene products, electroplating, etc. For the first time, effects of SLS as an electroyte additive on electrochemical behavior of positive active material and commercial positive plates have been studied by cyclic voltammetry (CV), eletrochemical impedance measurements. The electrode surface morphology after 20 cycles of CV was studied by using scanning electron microscopy (SEM). Results show that SLS additive significantly improves the conversion reactions of positive active material and therefore enhances charge/discharge capacity. By increasing SLS concentrate, crystalline structure of positive active material changed. The effects of SLS on kinetic parameters of positive electrode reactions are also discussed in this paper. The results showed that SLS is promising for use as electrolyte additive for lead- acid batteries.

Keywords: lead-acid battery, positive plate, positive active material, electrolyte aditive, sodium lauryl sulfate.

1. INTRODUCTION

Lead acid battery is a long-standing traditional source of power, with many outstanding features such as high electrity, stable operation, small inert resistance, simple structure, low cost, etc. Lead acid batteries are widely used for starting, lighting, ignition (SLI) batteries, backup power supply, etc, resulting in annual turnovers of lead acid battery industry reached tens of billions of US dollars on a worldwide basis [1]. Nevertheless, the positive active material of lead acid battery has a comparatively low coefficient of utilization. It is only about 45 to 50 % for discharge with small current density. Therefore, how to raise the coefficient of utilization of the positive active material has become one of the problems that arouses continuous concern among scientists and engineers that are working in field of chemical power sources [2].

Many approaches have been done to overcome this disadvantage such as: adding organic materials in positive paste [2 - 4] and using additives in electrolyte solution. The latter approache is very effective without changing the production process. Voss [5] and Meissner [6] have published comprehensive assessments of effects of H_3PO_4 and phosphate salts on activity of lead acid batteries. Accordingly, the addition of H_3PO_4 to the electrolyte extends the cycling life, decreases the irreversible sulfation of positive active material. The addition of H_3BO_3 at concentration up to 0.4 % inhibits the formation of hard-$PbSO_4$ and reduces the self-discharge of the PbO_2 electrode. Naima Boudieb et al. [7 - 9] have studied effects of two phosphate surfactances on electrochemical behavior of lead acid batteries. Results showed that those additives have some beneficial effects on performance of battery.

Sodium lauryl sulfate (SLS) is an anionic surfactant used in many applications such as cleaning and hygiene products, electroplating, etc. In this paper, for the first time, effects of SLS as an electroyte additive on electrochemical behavior of positive active material and commercial positive plates have been studied.

2. EXPERIMENTAL

2.1. Preparation of working electrode

The working electrode is a flat plate made of pure lead metal or a commercial positive plate taken from a 5Ah-type battery. Except that working surface area of electrodes was exposed, the sides and other parts of them were covered with an epoxy to avoid any contact with electrolyte solution. Then, electrodes were polished with smooth paper.

2.2. Materials and electrolytes

The 98 % concentrated sulfuric acid and sodium lauryl sulfate is the pure chemical from China. The H_2SO_4 electrolyte (d = 1.27 $g.cm^{-3}$) was prepared from concentrated H_2SO_4 and double distilled water. Electrolyte solutions containing 10, 50, 100, 150, 200, 250 and 300 $mg.L^{-1}$ of SLS additive were prepared by adding an appropriate calculated amount of SLS additive to the electrolyte.

2.3. Electrochemical measurements

Electrochemical measurements were carried out with a potentiostat/galvanostat equipment (AUTOLAB PGSTAT 302N-Netherlands) using the three electrode system. Working electrodes were pure lead and commercial positive electrode. The counter electrode and reference electrode were a pure lead sheet and Al/AgCl electrode, respectively. Before every mesurement, the working electrode was mechanically polished with emery paper and cleaned with acetone and double distilled water.

Cyclic voltammograms were obtained at a 50 $mV.s^{-1}$ scan rate, between 1.14 and 2.5 V (Ag/AgCl) for pure lead electrode and 1.14 to 2.1 V (Ag/AgCl) for commercial positive electrode. The used working electrode has a surface area of 0.57 cm^2 for pure lead electrode and 0.13 cm^2 for commercial positive electrode.

Electrochemical impedance spectroscopy measurements were carried out after 20 cycles of CV of the lead electrode in the solution to reach a steady-state condition. The frequency range was set from 10 kHz to 10 mHz with potential amplitude of 5 mV in open circuit potential.

2.4. SEM imaging

Micrographs of pure lead alloy electrode were obtained with JSM 6610- LA scaning electron microscopy (Jeol- Japan). To determine the microstructure of $PbSO_4$ and PbO_2 formed on electrode surface, before taking SEM imaging, electrodes were polarized by CV with 20 cycles.

3. RESULTS AND DISCUSSION

3.1. The conversion of specials in positive active material.

Figure 1 shows cyclic voltammograms recorded at 50 mV.s^{-1} scan rate on a pure lead electrode in H_2SO_4 (d = 1.27 g.cm^3) with and without various additive concentrations of SLS, the potential region from 1.14 to 2.5 V (Ag/AgCl). It is clear that there are two peaks in CVs. The anode peak relates to the oxidation of lead sulfate to lead dioxide and the other peak relates to the reduction of lead dioxide to lead sulfate corresponding to the following reaction equation:
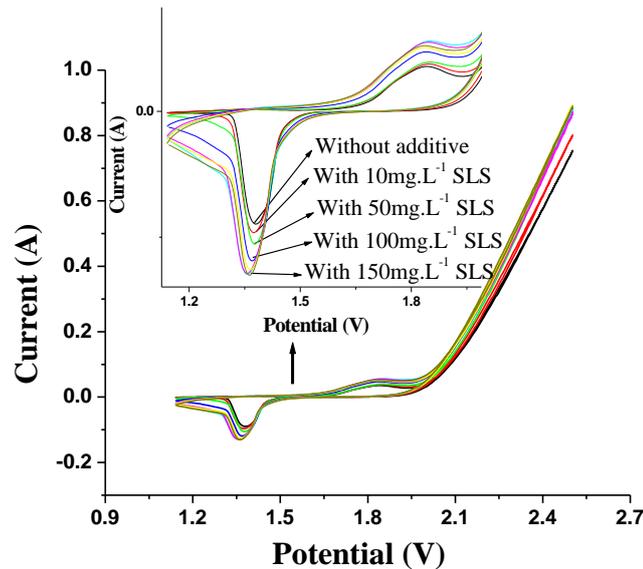
$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \leftrightarrow PbSO_4 + 2H_2O \qquad (1)$$

Figure 1. Cyclic voltammograms of pure lead electrode in H_2SO_4 (d = 1.27g.cm^{-3}) with and without SLS in 20th cycle, Scan rate: 50mV.s^{-1}.

The obtained data from Fig. 1 are gathered in Table 1. E_{pa} and E_{pc} (mV) are anode and cathode potentials, respectively. ΔE_p (mV) is the difference between anode and cathode potential values, which is characteristic for reversible degree of electrode reaction. Q_{add}^+ / Q_0^+ and Q_{add}^- / Q_0^- are coefficients used to evaluate the conversion level of lead sulfate to lead dioxide and vice versa, respectively. They are quotient of charge amount (the area under peaks) used for lead sulfate oxidation (Q^+) or lead dioxide reduction (Q^-) in 20th cycle.

From Table 1, ΔE_p values of pure lead electrode in absence of SLS additive is smaller than that in presence SLS additive. This indicates that the addition of SLS additive to make

conversion reactions on alloy electrode become more irreversible. The more SLS additive concentration from 10 to 200 mg.L^{-1}, the more decreasing reversible degree of reactions on the electrode is. Then, with continued increase in SLS additive concentration of over 200 mg.L^{-1}, the reversible degree of electrode reactions increases again.

Table 1. Influence of SLS additive concentration on conversion of $PbSO_4$ to PbO_2 and vice versa on pure lead electrode.

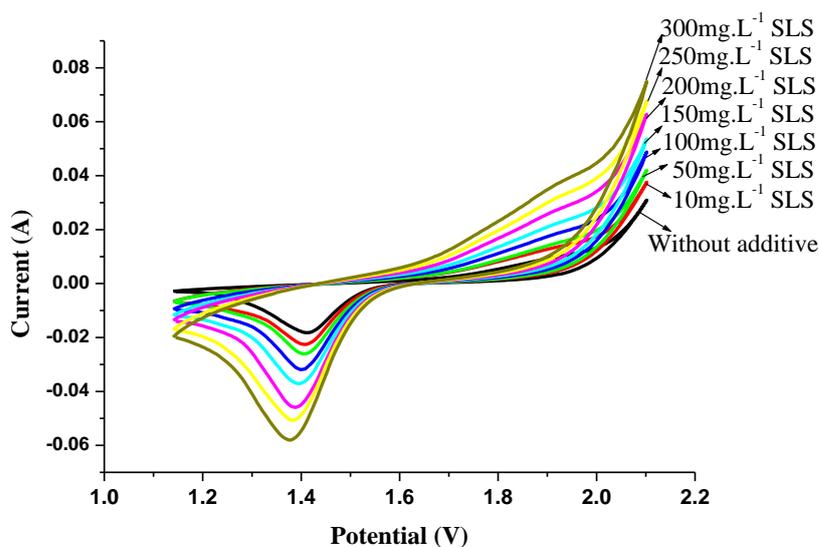| C_{SLS} (mg.L^{-1})	E_{pa} (mV)	E_{pc} (mV)	ΔE_p (mV)	Q_{add}^+ / Q_0^+	Q_{add}^- / Q_0^-
0	1843	1379	464	1	1
10	1843	1374	469	1.146	1.114
50	1853	1379	474	2.106	1.229
100	1843	1369	474	2.380	1.488
150	1848	1360	488	2.782	1.730
200	1848	1360	488	2.704	1.673
250	1838	1365	473	2.810	1.521
300	1843	1365	478	2.699	1.559

Figure 2. Cyclic voltammograms of commercial positive electrode in H_2SO_4 (d = 1.27g.cm^{-3}) solution with and without SLS in 20th cycle, Scan rate: 50 mV.s^{-1}.

As indicated from Table 1, values of conversion coefficients with the presence of SLS in electrolyte solution are greater than one. This shows that SLS additive significantly improves conversion reactions of positive active material, especially at SLS concentration range of 150 to 200 mg.L^{-1}.

A similar behavior is also recognized from cyclic voltammetry measurements on the commercial positive electrode in H_2SO_4 solution with and without SLS additive (Fig. 2).

4

Reduction peaks are clearly observed while oxidation peaks are overlapped by the oxygen release.

It is well known that, a cycle of cyclic voltammetry measurement can be considered as a charge and discharge cycle for surface material layer of electrode. This reveals that SLS additive with the ability to significantly improve the conversion of positive active material can be increase the capacity of positive electrode. Thus, SLS is suitable for use as an additive for electrolyte in lead acid batteries.

3.2. Effect of SLS additive on kinetic parameters of conversion reaction.

Figure 3 shows electrochemical impedance spectroscopys in Nyquist plots of pure lead electrode in H_2SO_4 solution without and with various concentrate of SLS, and an equivalent circuit using to fit the experimental data.
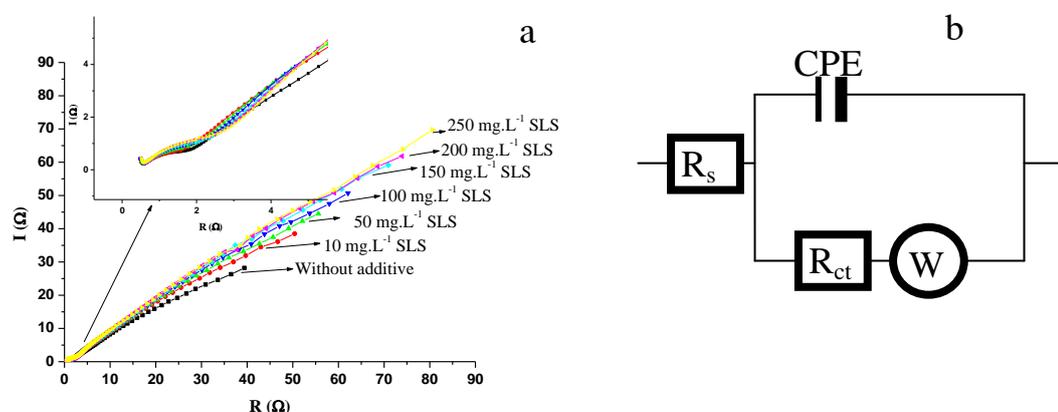

Figure 3. The electrochemical impedance spectroscopys in Nyquist plots (a) and equivalent circuit (b) of pure lead electrode in H_2SO_4 solution without and with various concentrates of SLS.

Table 4. Electrochemical parameters of conversion reaction in Pb-Sb alloy electrode obtained by impedance measurements.

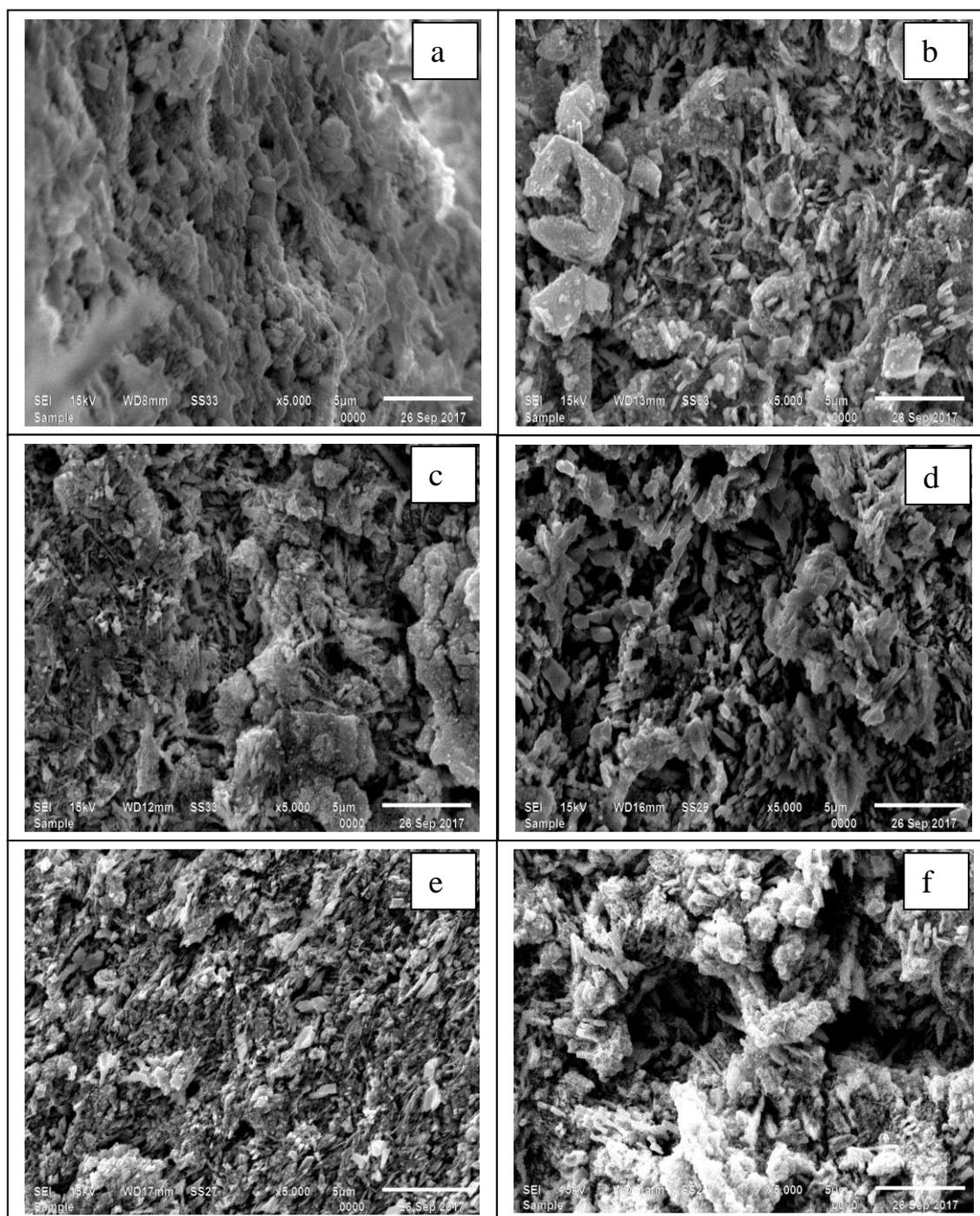| Parameters	Concentration of SLS (mg.L^{-1})						
	0	*10*	*50*	*100*	*150*	*200*	*250*
R_s (mOhm)	133	128	121	118	112	110	100
CPE (mF)	28.33	17.08	15.38	13.98	11.95	12.02	10.59
R_{ct} (mOhm)	2.072	1.183	1.235	1.297	1.397	1.414	1.451
σ_1 (mDW)	57.56	47.00	40.34	35.84	34.03	30.21	29.75

Figure 4. The scanning electron micrographs (SEM) of pure lead electrode after 20 cycles of CV in
H$_2$SO$_4$ solution without SLS (a) and with SLS concentrates of 10 mg.L^{-1} (b), 50 mg.L^{-1} (c),
150 mg.L^{-1} (d), 200 mg.L^{-1} (e), 250 mg.L^{-1} (f).

The kinetic parameters of conversion reaction in positive active material drawn by fitting the measured impedance data to the equivalent circuit. In this particular, R$_s$ is the solution resistance, CPE represents the constant phase element which is substituted for double-layer

6

capacitance, R_{ct} is the charge transfer resistance, W stands for the diffusion impedance in the double layer. The results of fitting with equivalent circuit are listed in a Table 4.

From table 4, it can seen that the value of charge transfer resistance in the presence of SLS additive is smaller than that in absence of SLS additive. However, with increasing in SLS concentrates from 10 to 250 mg.L^{-1}, the value of R_{ct} increases. The beneficial effect of SLS additive on the charge transfer process seems to be the result from crystallographic orientation of SLS additive.

It is known that the Warburg factor σ characterizes for the ability to interfere with the diffusion of reactants and reaction products. This is important because the delay in diffusion of them increases the concentration polarization and makes reaction process more difficult. Notice that the values of the Warburg factor of pure lead electrode in electrolyte without SLS additive is larger than that with SLS additive. This can be explained by the fact that, when added to the electrolyte solution, the SLS additive adsorbs to the electrode surface and contributes to the formation of a semipermeable membrane. The present of SLS in the formed semipermeable membrane reduces the porosity of the membrane. As a consequence, the transition of specials through the membrane and double-layer are impeded.

From Table 4, values of R_s and CPE decrease in presence of SLS additive. This indicates that the addition of SLS in H_2SO_4 solution decreases resistance of electrolyte and changes structure of double layer.

The reduction of charge transfer resistance and the increase of diffusion impedances explain the effect of SLS additive on conversion reactions, as discussed above.

3.3. The surface morphology of alloy electrode

Figure 4 shows SEM surface images of pure lead electrode after 20 cycles of CV in H_2SO_4 solution with and without various concentrations of SLS, respectively. Durring CVs, the conversion between PbO_2 and $PbSO_4$ occus on the surface of positive electrode arcording to reaction (1). As indicated from Fig. 4, formed crystals $PbSO_4$ and PbO_2 on the pure lead electrode surface in the presense of SLS additive are smaller in size and more spongy. It seem that SLS additive adsorbed on electrode surface, hence, changed the structures of crystals formed on the electrode surface.

4. CONCLUSIONS

The effects of SLS on electrochemical behavior of positive active material and commercial positive electrode were investigated. The following conclusions were drawn:

i) The presence of SLS in electrolyte solution significantly improves the conversion reactions of both positive active material and commercial positive electrode and thus increases their discharge/charge capacity. However, the SLS additive makes electrode reactions become less reversible.

ii) The effects of SLS additve on conversion reactions of positive active material are the result of reduction of charge transfer resistance, change of double layer and increase of diffusion impedance.

iii) The addition of SLS in electrolyte solution changed surface morphology of positive electrode. The formed $PbSO_4$ and PbO_2 crystals are smaller in size and more spongy.

iv) The electrochemical behavior of positive active material and commercial positive electrode depends on SLS concentration in the electrolyte. The SLS additive is promising for use as suitable additives for lead- acid batteries.

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