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Electrochemical behavior of lead acid battery alloys in the presence of different surfactant additives in the electrolyte

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The present study focuses on the elucidation of the basic effects of sodium dodecyl sulfate (SDS) or cetyltrimethyl ammonium bromide (CTAB) as electrolyte additives on the electrochemical reactions proceeding on a lead electrode immersed in 4.5M H_2SO_4 solution by applying linear sweep voltammetry (LSV) measurements in the $PbSO_4$ / PbO_2 potential region. The lead electrodes are manufactured from pure Pb (99.99%), Pb-Ca-Sn or Pb-Sb alloys. Addition of SDS or CTAB to the electrolyte seems to improve the discharge capacity of the anodic layer. For Pb-Sb electrodes immersed in solutions containing the investigated organic substances the capacity increases with increase of the cycle number and high values are recorded. The presence of alloying elements and studied electrolyte additives affects the processes that occur on the positive electrode surface at open circuit conditions and changes the rate of PbO_2 reduction and the mode of lead sulfate deposition.

Keywords: lead acid battery, lead electrode, surfactant, linear sweep voltammetry

INTRODUCTION

Production and use of lead acid batteries (LABs) continues to grow due to new applications such as energy storage for renewables, remote telecommunications, micro-hybrid electric vehicles, emergency power supply for computers, lighting and security systems. A wide range of inorganic and organic materials are used as additives to the electrolyte or/and to the negative and positive electrodes of LABs with the aim to improve their conductivity, enhance battery capacity and cycle life, reduce hydrogen and oxygen evolution reactions on the negative and positive electrodes, reduce electrode corrosion, increase reversibility of $PbSO_4$ crystals during charge discharge processes, etc. [1].

Pure lead or lead alloys are used for lead acid battery grids, straps, terminal posts and external connectors because of their high corrosion resistance and high electrical conductivity. Lead-antimony (Pb-Sb) and lead-calcium-tin (Pb-Ca-Sn) alloys are used for the production of various lead-acid batteries [2, 3]. Previous works have established that the use of a Pb-Sb alloy (e.g. for positive starting lighting and ignition (SLI) battery grids) enhances the hydrogen and oxygen evolution reactions during charging, leading to water loss [4-6]. Low antimony alloys (containing 1-2.7% Sb) reduce the transfer of antimony to the negative plate and thus reduce water loss of battery, especially when combined with Pb-Ca negative grids. Pb-Ca alloys were introduced in the thirties of the 20th century [7] to reduce water decomposition and thus battery maintenance. On polarization within the $PbSO_4/PbO_2$ potential region, the surface of the positive electrode is oxidized and a corrosion layer (CL) forms comprising a variety of oxides $Pb/PbO/PbO_n/PbO_2$ ($1<n<2$). Monahov and Pavlov [8] have established that antimony from the alloy gets incorporated in the CL and may thus improve the electrical and mechanical contact between the CL and the positive active mass, and eventually enhance the energetic performance of the lead acid cell. Slavkov *et al.* [9] have reported that Pb-Ca-Sn alloys exhibit increased corrosion rate as compared to pure lead. Many research studies have been conducted to modify the composition of Pb-Ca-Sn alloys [2, 10-13] with the aim to overcome this disadvantage and enhance the electrochemical performance of the electrode in H_2SO_4 solution.

Different types of inorganic substances, like H_3PO_4, H_3BO_3, $SnSO_4$, Na_2SO_4, have been extensively studied and reported as beneficial electrolyte additives that improve the cycle life of LABs and suppress the hydrogen and oxygen evolution reactions [14-22].

Surfactants are substances that lower the surface tension of two–phase systems due to adsorption at the surface. For application in LABs surfactants should be stable in highly concentrated H_2SO_4 solutions at high anodic potentials.

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A number of organic additives have been examined and their potential to improve the capacity and cycle life or suppress the gas evolution reactions and water loss of LABs has been evaluated [23-29]. Ghavami *et al*. [30] have investigated the effect of surfactants on the sulfation of lead acid cell negative electrodes and have reported that sodium dodecyl sulfate surfactant (SDS) improves the cycle life and fine $PbSO_4$ crystals are formed, while cetyltrimethyl ammonium bromide (CTAB) surfactant exerts the opposite effect on the crystal morphology of the negative active mass.

The focus of the present study is to elucidate the basic effects of SDS and CTAB as electrolyte additives on the electrochemical reactions proceeding on a lead or lead alloy positive electrode immersed in 4.5M H_2SO_4 solution by applying electrochemical methods in the $PbSO_4/PbO_2$ potential region.

EXPERIMENTAL

Electrochemical experiments

Test cell design for investigation of positive electrode properties. A three-electrode small cell setup was used to study the behavior of lead or lead alloy electrodes. A small Pb (99.99% purity) or Pb-1.8Sb-Se or Pb-0.06Ca-1.25Sn sheet embedded in epoxy resin was used as working electrode. The smooth model electrode geometrical area exposed to the electrolyte was 0.5 cm^2. A bit bigger Pb (99.99% purity) sheet with 2.5 cm^2 exposed area was used as counter electrode. These electrodes were assembled in a small cell and 50 ml of 4.5 M H_2SO_4 solution with different surfactants was added. The types of studied substances and their loading concentrations in the electrolyte are summarized in Table 1. Sulfuric acid (95-98%), SDS (> 98.5%) and CTAB (> 99%) were delivered by Sigma-Aldrich. The reference electrode used was Hg/Hg_2SO_4. The obtained results for the thus prepared test cells were compared with those for a control cell with blank electrolyte (with no surfactant additive).

Cyclic voltammetry measurements. As a first step of the test, the Pb or Pb alloy model smooth working electrode was set to cathodic electropolishing at a potential of -1.30 V (*vs*. Hg/Hg_2SO_4) for 30 min to reduce all Pb (II) compounds on its surface and then anodically polarized at +1.70 V for another 30 min. Then, the different test electrodes were subjected to cyclic voltammetry measurements in the $PbSO_4/PbO_2$ potential range from +0.70 to +1.50 V (*vs*. Hg/Hg_2SO_4) at a scan rate of 10 $mV.s^{-1}$ for 600 cycles.

$PbO_2/PbSO_4$ electrode - open circuit tests. The tested electrodes were cleaned in the above mentioned manner and then subjected to anodic polarization at +1.70 V for 1 hour. The potential value of +1.70 V was chosen, because it would ensure the formation of PbO_2 on the positive lead acid battery grid. The test electrodes were left on open circuit in 4.5M H_2SO_4 solution with/without surfactant for 90 h and the potential *vs*. time curves were recorded.

All electrochemical tests were performed with ARBIN Instrument BT2043 potentiostat/ galvanostat at a temperature of 25°C.

Scanning electron microscopy (SEM) measurements. The morphology of the lead sulfate crystals was observed on a JEOL 200 CX scanning electron microscope.

RESULTS AND DISCUSSION

Cyclic voltammetry measurements

The charge/discharge reactions of $PbSO_4/PbO_2$ electrodes were studied by cyclic voltammetry between +0.70 V and +1.50 V at a scan rate of 10 mV. s^{-1}. A total of 600 cycles were conducted. The recorded voltammograms feature a continuous increase in the anodic and cathodic currents with cycling. This indicates that a greater amount of Pb is converted to PbO_2 and $PbSO_4$ with cycling.

Figure 1 presents the recorded cyclic voltammetry curves for Pb or Pb-alloy electrodes in 4.5M H_2SO_4 in the presence or absence of different ionic types of surfactants at the 600^{th} cycle of the test. The data in Fig. 1 show that the current peaks of both the oxidation and the reduction reactions are influenced by the electrode material and by the type of surfactant, too.

Table 1. Types of selected surfactants and loading concentrations in the electrolyte

Electrolyte additive	Chemical formula	Ionic type	Molecular weight	Loading, %
Sodium dodecyl sulfate (SDS)	$NaC_{12}H_{25}SO_4$	anionic	348.48	0.12
Cetyltrimethyl ammonium bromide (CTAB)	$C_{19}H_{42}BrN$	cationic	364.45	0.024

Comparing the recorded voltammograms it can be clearly seen that the organic substances added to the electrolyte have similar effects on the redox reactions on all tested electrodes. The anodic peaks related to the oxidation of lead to various oxides $PbO/PbO_n/PbO_2$ ($1< n <2$) for the different types of electrodes and for blank and/or organic-substance-doped solutions appear at potentials within the potential interval from 1.09 V to 1.22V.

The voltammogram for pure Pb electrode (Fig. 1a) indicates that the anodic peak for the blank or the SDS-doped solution appears at a potential value of +1.22 V. In the presence of the surfactant CTAB, the peak potential shifts in the negative direction. The anodic peaks for the lead alloy electrodes (in blank or organic-substance-doped solutions) appear at more negative potentials, e.g. at 1.09 V (Fig.1b) for Pb-Sb and at 1.18 V for Pb-Ca-Sn (Fig. 1c), except for the Pb-Ca-Sn electrode in the presence of SDS surfactant.

The cathodic peak or peaks are related to the reduction of lead dioxide to lead sulfate. The voltammograms for pure Pb or Pb-Ca-Sn electrodes feature analogous cathodic branches, while the Pb-Sb electrode produces cathodic peaks with much higher values. The cyclic voltammetry curves for Pb (Fig. 1a) and for Pb-Ca-Sn (Fig. 1c) contain two cathodic peaks for blank and surfactant-doped solutions (at 1.07 V and at 0.90 V), while the Pb-Sb electrode yields a single cathodic peak for all solutions at 1.07 V. The reaction of PbO_2 reduction to $PbSO_4$ for pure Pb or Pb-Ca-Sn electrodes is more strongly affected by the presence of CTAB additive in the electrolyte.

Figure 2 presents the discharge capacity (amount of cathodic electricity) values calculated from the integration of the surface area of the cathodic peak corresponding to the reduction of PbO_2 to $PbSO_4$ for the different experimental electrodes.

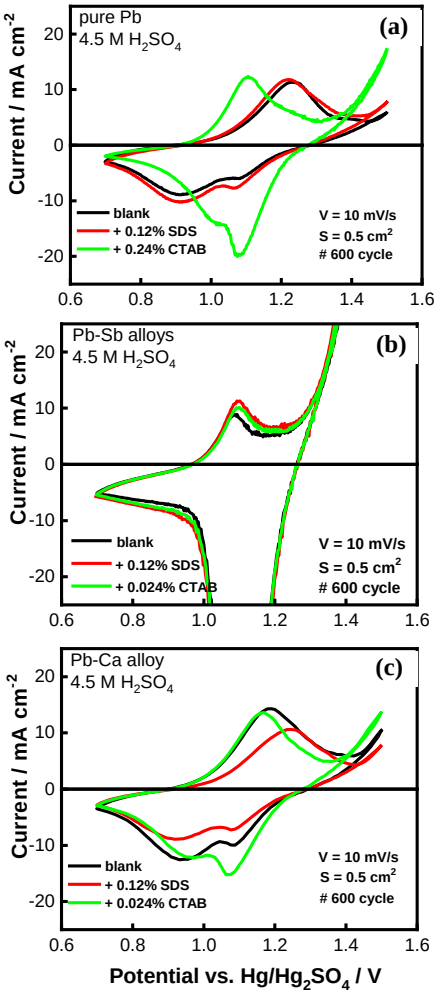

Figure 1. Cyclic voltammetry curves for tested electrodes in blank or surfactant-doped solutions, recorded at the 600th cycle in the region from +0.70 V to +1.50 V: (a) pure Pb electrode, (b) Pb-Sb alloy electrode and (c) Pb-Ca-Sn alloy electrode.

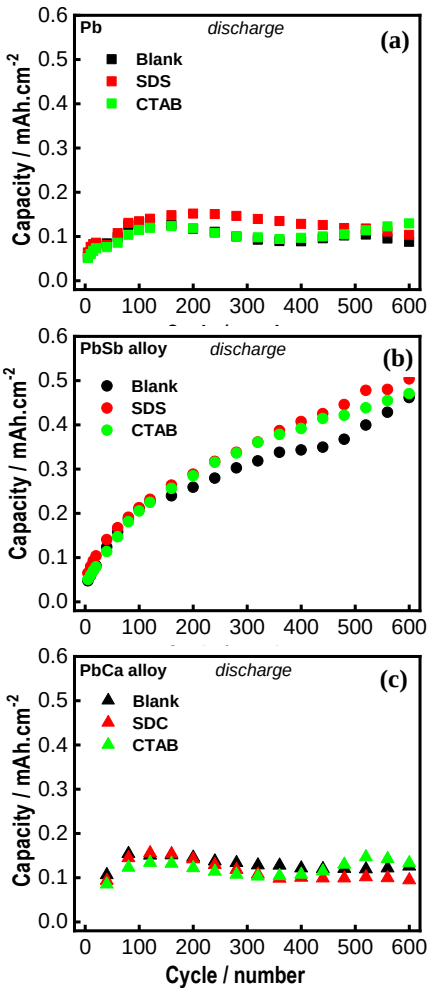

Figure 2. Capacity of tested electrodes *vs.* cycle number in blank or surfactant-doped solutions: (a) pure Pb electrode, (b) Pb-Sb alloy electrode and (c) Pb-Ca-Sn alloy electrode.

The organic surfactants in the solution exert similar influence on the capacity for pure lead or lead alloy electrodes (Figs. 2a, 2b, 2c). For Pb-Sb electrodes immersed in solutions containing the investigated organic substances the capacity increases with increase of the cycle number and high values are recorded (Fig. 2b). This experimental finding is in agreement with the well-known positive effect of antimony on lead acid battery positive grid performance, where antimony is incorporated into the corrosion layer and thus allows the grid to recover from deep discharge by impeding the formation of $PbSO_4$ insulating layer between the active mass and the grid, and thus enhances the energetic performance of the lead acid cell.

Open circuit tests

During the open circuit stay, self discharge reactions proceed, and the reduction of PbO_2 to PbO_n and/or $PbSO_4$ takes place at a slow rate.

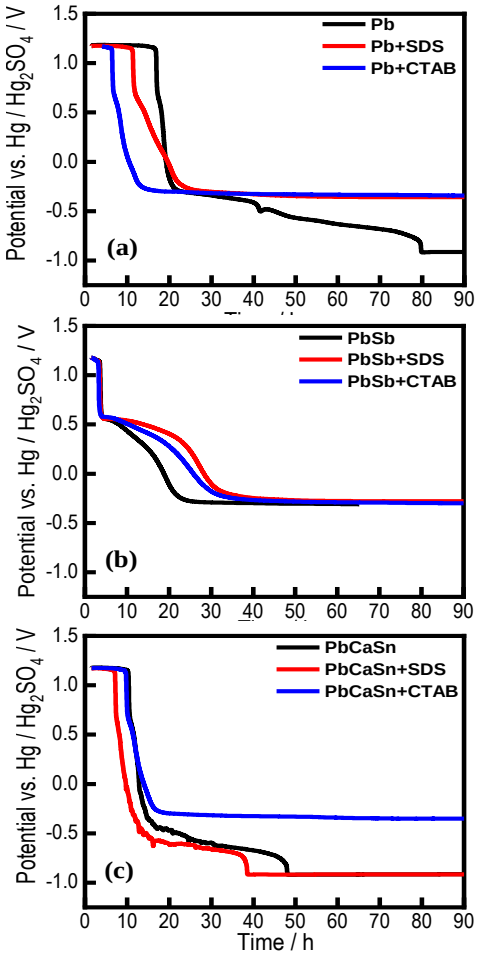

Figure 3. Open circuit experiments for 90 h: (a) pure Pb electrode, (b) Pb-Sb alloy electrode and (c) Pb-Ca-Sn alloy electrode.

Figure 3 presents the recorded potential *vs.* time curves at open circuit conditions. The recorded potential of the tested electrode in 4.5M H_2SO_4, in the presence or absence of the selected surfactants, at open circuit condition is the potential at which the cathodic and anodic reaction rates are in equilibrium and the system is in a steady state. It can be clearly seen from the curves in Fig. 3 that an initial time period appears at 1.176 V before a potential decay for all tested electrodes is registered. This initial period is attributed to the PbO_2/$PbSO_4$ electrode system. As can be seen from Fig. 3, the time period in blank or surfactant-doped solution in the case of Pb-Sb electrodes is the shortest one (about 2 hours), against 5-16 hours for pure Pb electrodes and 7-10 hours for Pb-Ca-Sn electrodes. It can be concluded that the Sb alloying element and/or surfactant in the electrolyte change the rate of PbO_2 reduction and/or change the mode of lead sulfate deposition.

Based on the previous investigation, Pavlov [1, 31] concluded that three electrode systems form during anodic polarization of Pb electrode in H_2SO_4 solution, comprising: (i) *$Pb/PbSO_4$ system* - stable at potentials from -0.97 to -0.40 V (*vs.* Hg/Hg_2SO_4); (ii) *$Pb/PbO/PbSO_4$ system* - stable in the potential range from -0.40 to +0.95 V; (iii) *Pb/PbO_2 system* - formed at potentials above +0.95 V and containing α- and β-PbO_2. Table 2 presents the steady-state potentials and the respective electrode systems for the electrodes under test. These data show that all Pb-Sb test electrodes, Pb electrode in surfactant-doped solutions or Pb-Ca electrode in solution doped with CTAB may contain PbO phase on the electrode surface at steady-state potential that is more easily converted to PbO_2 under charge conditions and thus may enhance the energetic performance of the electrode. For Pb-Sb electrodes, this is in agreement with the experimental data in Fig. 2b.

SEM observation

The SEM microphotographs in Fig. 4 illustrate the morphology of the lead sulfate deposits formed on the surface of the test electrodes after open circuit stay in blank solutions or in solutions with added selected organic surfactants. The morphology of the crystals evidences that the presence of the selected surfactants and alloying elements has a noticeable effect on the $PbSO_4$ crystallization processes and thus, they might change the electrochemical properties of the electrode/electrolyte interface.

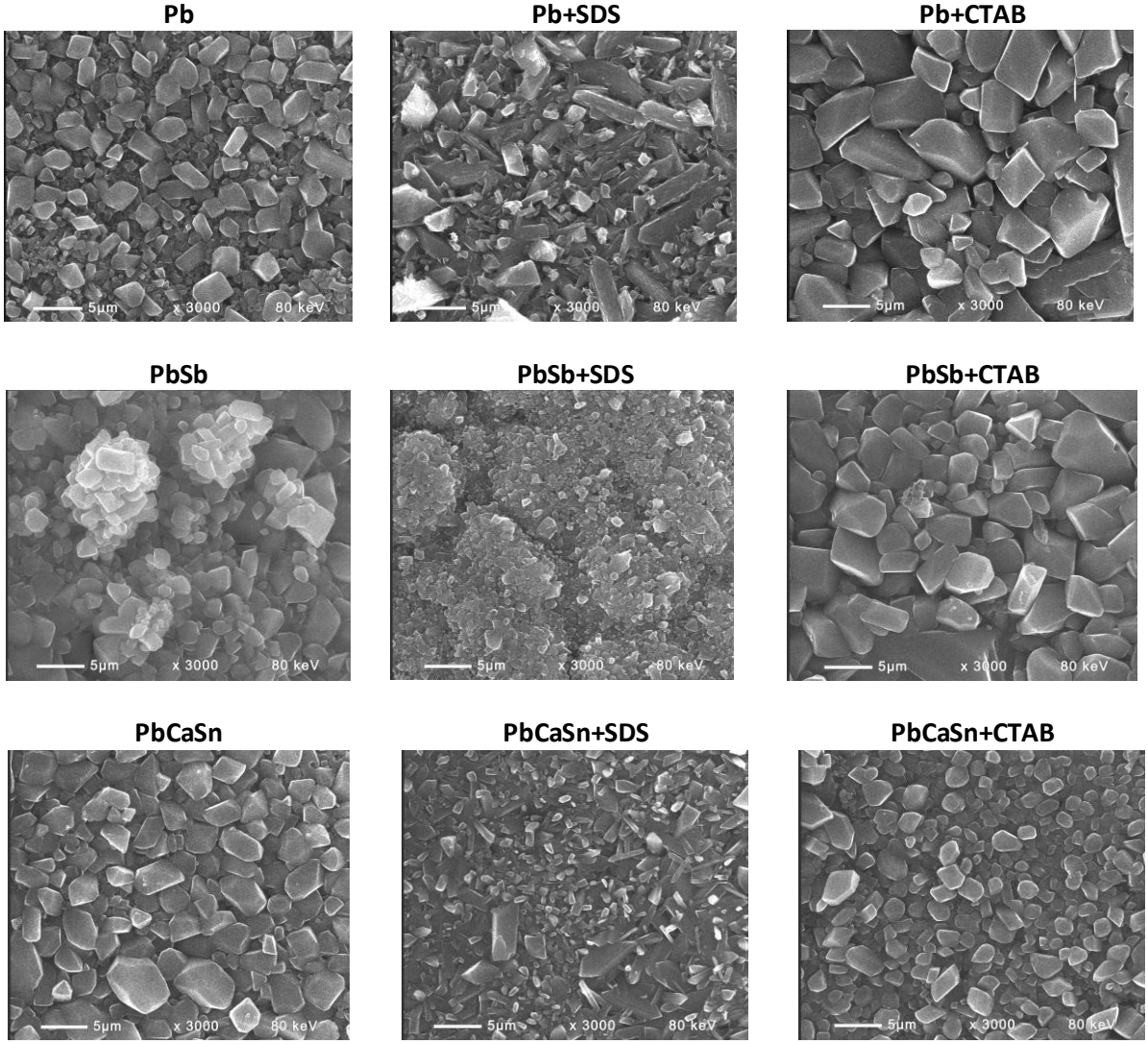

Figure 4. SEM microphotographs of the surface of the tested electrodes after open circuit stay

Table 2. Steady-state potentials and electrode systems for the test electrodes on open circuit stay

Electrode/ solution	O.C. potential, V	Electrode system
Pb blank	-0.9144	*Pb/PbSO₄*
Pb +SDS	-0.3579	*Pb/PbO/PbSO₄*
Pb+CTAB	-0.3437	*Pb/PbO/PbSO₄*
Pb-Sb blank	-0.3105	*Pb/PbO/PbSO₄*
Pb-Sb +SDS	-0.2798	*Pb/PbO/PbSO₄*
Pb-Sb+CTAB	-0.3006	*Pb/PbO/PbSO₄*
Pb-Ca-Sn blank	-0.9146	*Pb/PbSO₄*
Pb-Ca-Sn +SDS	-0.9154	*Pb/PbSO₄*
Pb-Ca-Sn+CTAB	-0.3517	*Pb/PbO/PbSO₄*

The deposits formed on the Pb or Pb-Sb electrodes in solutions with CTAB additive contain the largest particles sized about 5 to 10 micrometers, against 3-4 micrometer-sized particles formed on the Pb-Ca-Sn electrode in the acid solution with the same surfactant.

Smaller crystals are observed in the layer formed in blank solutions with no organic additives. The smallest crystals (about 0.1 micrometer in size) interconnected in agglomerates are observed in the deposit formed on the Pb-Sb electrode in SDS-doped solution. This indicates that, in the latter acid solution, $PbSO_4$ particles are stabilized by the additive at a smaller size and do not easily recrystalize. On the other hand, the deposits formed on the Pb or Pb-Ca-Sn electrodes in SDS-doped solution comprise $PbSO_4$ crystals with different shape and size. Addition of SDS to the electrolyte causes the formation of mixed-type crystals, e.g. prismatic shaped particles about 5 micrometers in size and smaller particles sized about 1 micrometer.

CONCLUSIONS

The study of the basic effects of SDS or CTAB organic surfactants on the $PbO_2/PbSO_4$ electrode reactions on Pb, Pb-Sb and Pb-Ca-Sn alloys shows that the addition of the selected substances in the electrolyte has a beneficial effect on the capacity of the test electrodes. For Pb-Sb electrodes immersed in solutions containing the investigated organic substances the capacity increases with increase of the cycle number and high values are recorded.

The reaction of PbO_2 reduction to $PbSO_4$ for pure Pb or Pb-Ca-Sn electrodes is more strongly affected by the presence of CTAB additive in the electrolyte.

The presence of alloying elements and studied electrolyte additives affects the processes that occur on the positive electrode surface at open circuit conditions. Antimony used as grid alloying element changes the rate of PbO_2 reduction and the mode of lead sulfate deposition.

The morphology of the crystals evidences that the presence of the selected surfactants has a noticeable effect on the $PbSO_4$ crystallization processes and thus they might change the electrochemical properties of the electrode/ electrolyte interface.

REFERENCES

1. D. Pavlov, Lead-Acid Batteries: Science and Technology, Second edn., Elsevier, 2017.
2. R. D. Prengaman, *J. Power Sources*, **95**, 224 (2001).
3. R. D. Prengaman, *J. Power Sources*, **158**, 1110 (2006).
4. B. Rezaei, S. Damiri, *J. Solid State Electrochem*., **9**, 590 (2005).
5. M. Shiota, T. Kameda, K. Matsui, N. Hirai, T. Tanaka, *J. Power Sources*, **144**, 358 (2005).
6. W. R. Osorio, C. S. C. Aoki, A. Garcia, *J. Power Sources*, **185**, 1471 (2008).
7. H. E. Haring, U. B. Thomas, *Trans. Electrochem. Soc.*, **68**, 293 (1935).
8. B. Monahov, D. Pavlov, *J. Electrochem. Soc*., **141,** 2316 (1994).
9. D. Slavkov, B. S. Haran, B. N. Popov, F. Fleming, *J. Power Sources*, **112,** 199 (2002).
10. R. K. Shervedani, A. Z. Isfahani, R. Khodavisy, A. Hatefi-Mehrjardi, *J. Power Sources*, **164,** 890 (2007).
11. H. T. Liu, J. Yang, H. H. Liang, J. H. Zhuang, W. F. Zhou, *J. Power Sources*, **93,** 230 (2001).
12. G. Lin, G. Zhou, D. Li, M. Zheng, *J. Rare Earths*, **24,** 232 (2006).
13. Y. B. Zhou, C. X. Yang, W. F. Zhou, H. T. Liu, *J. Alloys Compd*., **365**, 108 (2004).
14. S. Tudor, A. Weisstuch, S. H. Davang, *Electrochem. Technol.*, **5,** 21 (1967).
15. J. Burbank, *J. Electrochem. Soc.*, **111,** 1112 (1964).
16. B.K. Mahato, *J. Electrochem. Soc.*, **126,** 369 (1979).
17. E. Voss, *J. Power Sources*, **24**, 171 (1988).
18. H.A. Laitinen, N. Walkins, *Anal. Chem.*, **47,** 1353 (1975).
19. K. R. Bullock, *J. Electrochem. Soc.*, **126,** 1848 (1979).
20. E. Meissner, *J. Power Sources*, **67**, 135 (1997).
21. K. Saminathan, N. Jayaprakash, B. Rajeswari, T. Vasudevan, *J. Power Sources*, **160**, 1410 (2006).
22. C. Bemelmans, T. O'Keefe, E. Cole, *Bull. Electrochem.*, **12,** 591 (1996).
23. T. C. Wen, M. G. Wei, K. L. Lin, *J. Electrochem. Soc*., **137**, 2700 (1990).
24. Y. Sato, K. Hishimoto, K. Togashi, H. Yanagawa, K. Kobayakawa, *J. Power Sources*, **39,** 43 (1992)
25. Z. Shi, Y.-H. Zhou, C.-S. Cha, *J. Power Sources*, **70**, 205 (1998).
26. L. Torcheux, C. Rouvet, J.P. Vaurijoux, *J. Power Sources*, **78,** 147 (1999).
27. M. Ghaemi, E. Ghafouri, J. Neshati, *J. Power Sources*, **157,** 550 (2006).
28. A. Tizpar , Z. Ghasemi, *Appl. Surface Science*, **252,** 8630 (2006).
29. S. Hosseini, K. Farhadi, S. Banisaeid, *J. Energy Storage*, **7**, 121 (2016).
30. R. K. Ghavami, F. Kameli, A. Shirojan, A. Azizi, *J. Energy Storage*, **17**, 170 (2018).
31. D. Pavlov, N. Iordanov, *J. Electrochem. Soc*., **117**, 1103 (1970).