



Effects of surfactants on sulfation of negative active material in lead acid battery under PSOC condition



Robab Khayat Ghavami*, Fatemeh Kameli, Ali Shirojan, Amir Azizi

R & D Center, Tavan MFG. Co., P.O. Box 19575-361, Tehran, I.R., Iran

ARTICLE INFO

Article history:

Received 8 December 2015

Received in revised form 6 June 2016

Accepted 13 June 2016

Available online xxx

Keywords:

Lead-acid battery

Performance

Sulfation

Partial-state-of-charge regime

Surfactant

ABSTRACT

Lead–acid battery performance is severely limited to negative plate sulfation (irreversible formation of lead sulfate). The influence of surfactants types in lead-acid battery electrolyte has been investigated on the sulfation of negative active material (NAM) under high-rate partial-state-of-charge (HRPSOC) operation. However, it is still an open investigation to explore that how to make the lead sulfate crystals more electrochemically active and how surfactants affect on their pattern growth. This research demonstrates that various surfactants have different effects on NAM sulfation using XRD (X-ray diffraction), SEM (scanning electron microscopy), CV (cyclic voltammetry) and EIS (electrochemical impedance spectroscopy) techniques, which in some cases their behaviors are conversely. Amongst all tested surfactants, the cell with anionic sodium dodecyl sulfate surfactant (SDS) exhibits the longest cycle life with the least overcharge and fine PbSO_4 crystals. The cell with cationic cetyl trimethyl ammonium bromide (CTAB) surfactant shows opposite effects.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Irreversible formation of the lead sulfate in negative active material (NAM), which is called sulfation or hard sulfate, has plagued battery engineers for many years. It has also been a main cause of failures in lead–acid batteries. This type of lead sulfate cannot, or only partially, be returned to its electrochemically active state. Thus, a corresponding loss of capacity and hydrogen evolution take place in early stages of the charging. Usually, negative plates have more trends to be sulfated, than positive plates [1].

It is important to know that how the sulfation occurs in negative plates. The kinetic and mechanism of lead sulfate formation on the lead electrodes in sulfuric acid solution progress in three main mechanisms [2–5]: (a) dissolution-precipitation reaction [6] (b) solid-state mechanism [7] (c) a complex path way [8].

In order to avoid the formation of hard sulfate during cycling, the negative paste must be contained the expanders. Nowadays, advances in lead–acid batteries include the usage of additives and the modified charging methods to obtain the beneficial effect on the charge acceptance and the crystal morphology. The organic

expander component (lignosulfonate), being a surface active polymer, is adsorbed on the Pb surface and prevents the formation of a continuous PbSO_4 layer on the electrode surface [9]. The other expander component, barium sulfate, provides nuclei for the growth of numerous small PbSO_4 crystals, forming a porous layer instead of the continuous PbSO_4 film [10].

Many efforts have been performed on the development of several new features like stop-start cycling in micro hybrid vehicles, but this application requires battery that operates continuously at partial-state-of-charge (PSOC) condition and also to be charged and discharged at high rates (HRPSOC) [11–15]. Different methods were suggested e.g. addition of carbon black [16] and Bismuth material [17] electrochemical conversion of lead sulfate to lead which prepared from lead acetate and sodium sulfate solution in presence of SDS and poly(vinyl pyrrolidone) (PVP) [18] in order to overcome formation of large lead sulfate during cycling. Many researchers have reported that the adsorption of surfactants on the metal surface can markedly change the corrosion-resisting property of metal [19,20] that help to realize the relations between the adsorption and corrosion inhibition.

Surfactants have been widely applied in battery systems to improve the electrochemical performance through increment of the hydrogen evolution potential, inhibition of the metal corrosion and/or modification the crystals morphology. Surfactants with a long hydrophobic C—H chain and a hydrophilic head group can be

* Corresponding author.

E-mail address: robab.ghavami@gmail.com (R. Khayat Ghavami).

adsorbed at hydrophobic electrode surface. They change the electrode/solution interface properties that affect on the electrochemical process of electro active species [21,22]. According to Ritchie [23,24] and Willihnganz [25], the lead sulfate crystals with high porosity are formed during discharge as the consequence of partial coverage of lead sulfate by the organic material adsorption, while a limitation of the lead crystals size occurs during charge. It has been also found that presence of perfluorinated surfactant in positive active materials (PAM) cause excellent surface activity and/or cycle life [19]. In our previous researches [26,27], the influences of surfactants on performance characteristics of Zn-MnO₂ batteries was reported that their behaviors are very complex and depend on their concentration and negative or positive charged head groups of surfactants. It was found that the adsorption of surfactants on electrodes can have large effects on kinetic of electron transfer and consequently on the pattern growth of metal atoms.

With regard to behavior of the negative plates, which markedly affects on the PSoC service in lead-acid cells, the effect of surfactants (cationic cetyl trimethyl ammonium bromide (CTAB), anionic sodium dodecyl benzene sulfonate (SDBS), sodium dodecyl sulfate (SDS) and nonionic t-octyl phenoxy poly ethoxy ethanol (Triton X-100) are determined with the aim to suppress the accumulation of large lead sulfate to improve the performance of lead-acid cells under PSoC duty. The electrochemical characterizations are performed by cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS) in a three-electrode system. In this research, different techniques have been employed for characterization of negative electrodes such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) that proved to be particularly successful.

2. Experimental methods

2.1. Cell construction for investigation negative plate properties

Charge/discharge cycles were carried out in laboratory cells. All positive and negative plates and separators, which have been applied in this research, were furnished by Niru Battery Company. The negative electrode paste was prepared with 4.5% sulfuric acid/lead oxide ratio (75% degree of oxidation), 0.4% Vanispers-A, 0.8% BaSO₄ and 0.2% Carbon black and their grids are consist of Pb-0.09 wt% Ca-0.3 wt% Sn in (12 V sealed battery 3Ah) 12SB3 motorcycle battery.

The used flooded cells comprised of two positive and one negative plate with dimensions (68 mm *40 mm *2.9 mm as height, width and thickness, respectively) and poly vinyl chloride (PVC) as separator sheets. The nominal capacity of mentioned cell was 2.1 Ah when discharged at the 5-h rate (C5/5 = 2.1A.h). The amount of negative active materials in each electrode was about 28 g. Surfactant was added to electrolyte solution after formation. The cell was then charged fully with a constant current of 0.5 A for 10 h. A mercury/mercurous sulfate electrode was used as reference

electrode for measuring the potential of negative plate during cycling. All potentials were reported with respect to this electrode. A sulfuric acid electrolyte with 1.28 s.g. was used in this experiment. There was 1.89 cm³ of sulfuric acid solution for every gram of paste. The cells with different kinds of surfactant are presented in Table 1. The surfactant content in H₂SO₄ solution was determined 50 ppm that was below the critical micelle concentration point (CMC) for every surfactant. All electrochemical measurements and cycling tests were carried out by using battery test system, Solartron 1470A, at 25 °C.

Calculation of the conversion indicator is a rapid and useful procedure for investigation of additives affects on charging ability of negative plates, which is proposed by Lam [17]. Although the conversion indicator is not as same as charging efficiency, but these two parameters have a close relation. On the other hand, the higher conversion indicator causes to the greater charging efficiency. The conversion indicator refers to ratio between charge input (I_{ctp}) up to the turning point and the previous discharge capacity (I_{dt_d}) that can be calculated by the following equation:

$$I_{ctp}/I_{dt_d} \times 100\%$$

2.2. Cycling regimes Zero percent SoC/full-charge cycling and PSoC cycling regime

The effect of surfactant on the performance characteristic of the negative plate was determined from the performed initial capacity tests on cells. The negative plate was discharged at 2.2A (1 h rate) until the potential fell to -0.6V, which corresponds to state of charge (SoC0).

In PSoC cycling regime, the cells were successfully operated in 14 cycles through four different PSoC windows, respectively, 90–60%, 70–40%, 80–40% and 90–40%, (Fig. 1). In each PSoC window, the cell was discharged at 2.2A and recharged at 1.1A with an equal amount of charge input and charge output. End-of-discharge (EoD) and end-of-charge (EoC) potentials of the negative plates were recorded during cycling. The conversion indicator was determined for each cycle.

In PSoC operation, the battery cycles over a relatively small range centered on some intermediate state-of-charge, which causes PSoC operation to offer two major advantages.

1. It avoids the battery spending time near the gassing zone at top-of-charge.
2. It does not give rise to large volume change related stresses in the active masses [28].

2.3. Scanning electron microscopy(SEM)/X-ray diffraction(XRD)

The negative plates are rinsed with double distilled water to remove the H₂SO₄ and dried under vacuum with appropriate

Table 1
The specifications of different kinds of surfactants and their cells name.

| Surfactant | Kinds of surfactant | Concentration (ppm) | Abbreviated cell name | Molecular weight | Chemical formula | Critical micelle concentration (CMC) (mM) |
|--|---------------------|---------------------|-----------------------|------------------|---|---|
| Cetyl trimethyl ammonium bromide (CTAB) | cationic | 50 | CTAB-NAM | 364.45 | C ₁₉ H ₄₂ BrN | 1 |
| Sodium dodecyl benzene sulfonate (SDBS) | anionic | 50 | SDBS-NAM | 348.48 | C ₁₈ H ₂₉ NaO ₃ S | 1.6 |
| Sodium dodecyl sulfate (SDS) | anionic | 50 | SDS-NAM | 288.372 | NaC ₁₂ H ₂₅ SO ₄ | 8 |
| t-octyl phenoxy polyethoxyethanol (Triton X-100) | Non-ionic | 50 | TX-100-NAM | 647 | C ₁₄ H ₂₂ O (C ₂ H ₄ O) _n | 0.22–0.24 |
| Without surfactant | – | – | standard-NAM | – | – | – |

Download English Version:

<https://daneshyari.com/en/article/1133069>

Download Persian Version:

<https://daneshyari.com/article/1133069>

[Daneshyari.com](https://daneshyari.com)