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Short communication

The effects of different additives in electrolyte of AGM batteries on self-discharge

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Abstract

Hydrogen and oxygen evolution at the negative and positive electrodes in AGM batteries are the main reasons of self-discharging. The self-discharge of five AGM batteries was investigated by measuring different potential between two electrodes during 48 days. Five different battery electrolytes were used including 35% (w/w) H_2SO_4 without additives and the remaining contain 7.1, 9.94, and 21.3 $g\,l^{-1}$ sodium sulfate, 4 $g\,l^{-1}$ boric acid, 3 $g\,l^{-1}$ citric acid, and finally 0.7 and 1 $g\,l^{-1}$ stearic acid except one containing boric acid that the concentration of H_2SO_4 was 36% (w/w). The results revealed that the rate of self-discharge for battery without additive was 0.01 V day^{-1}. The battery with boric acid showed the lowest rate of self-discharge with 0.0025 V day^{-1}. It was also found that stearic and citric acids are comparatively appropriate additives for decreasing the self-discharge. They caused a decrease of the self-discharge rate to 0.005 and 0.0075 V day^{-1} on appropriate concentration, respectively. In compared to other additives, sodium sulfate showed to be not an appropriate additive for decreasing battery self-discharging. The rate of 0.03 V day^{-1} of self-discharging was obtained for the battery containing all selected concentration of sodium sulfate during first 4 days of measuring.

Keywords: Battery self-discharge; Open-circuit voltage; Additives

1. Introduction

When fully charged batteries are stored by suppliers or in the stores of the user then, depending on the type and characteristics of battery and other factors, such as storage time and temperature, the batteries will undergo a gradual process of self-discharge. The result is that when these batteries are called into the service they will not supply the design ampere-hour capacity that would be expected of a newly manufactured battery [1]. The effect of self-discharge reactions on the shelf life of the lead-acid battery was first reported in 1882, which reported that the process of self-discharge occurs slowly at room temperature [2]. It was claimed that increasing the temperature reduces the shelf life significantly [3]. The self-discharge reactions are well defined [4] and self-discharge rates in lead-acid batteries having immobilized electrolyte and limited acid volumes have been measured in several investigations [5–8]. Usually, the full capacity can be restored to the battery by subjecting it to a process of acclimatization whereby it is given a few charge/discharge cycles under controlled conditions. After a few such a cycles, the full capacity of the battery is usually restored [1], but this method is not suitable because it may cause battery overcharging and also this method has a maintaining cost.

From mechanistic point of view, the major contribution to self-discharge occurs at the negative electrode of a battery. Comparable self-discharge reactions at the positive electrode exist, but are of minor importance because all substances that may reduce the oxygen overvoltage markedly are oxidized at the extremely positive potential. Hydrogen evolution reaction cannot be suppressed completely even at the open-circuit cell voltage [9].

Self-discharge is a result of two reactions: an anodic one involving discharge of lead electrode and the cathodic of hydrogen evolution [3–10]:

$$Pb + HSO_4^- \Leftrightarrow PbSO_4 + H^+ + 2e^- \quad (1)$$

$$2H^+ + 2e^- \Leftrightarrow H_2 \quad (2)$$

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The reactions proceed at a mixed potential that is determined by the relative kinetics of both reactions. Hydrogen overvoltage determines the rate of the self-discharge reaction. A basic requirement for the lead-acid battery is that the overvoltage to be high [9]. Another self-discharge mechanism is oxygen evolution at the positive electrode. This mechanism also is a result of two reactions: a cathodic one involving discharge of the positive electrode and the anodic of oxygen evolution [3–10]:

$$H_2O \Leftrightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \tag{3}$$

$$PbO_2 + HSO_4^- + 3H^+ + 2e^- \Leftrightarrow PbSO_4 + H_2O \tag{4}$$

In sealed lead-acid battery with recombination of oxygen and hydrogen in the battery, to some extent the evolutions of gas decreases but during self-discharge the sulfation of plates increases and the equivalent water loss, so premature capacity loss (PCL) happens [11]. Oxygen recombination reaction also increases sulfation process of negative electrode [12,13]:

$$Pb + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow PbSO_4 + H_2O \tag{5}$$

The rate of the oxygen recombination reaction is depending on the rate at which the oxygen is diffused to the lead surface in the negative electrode. If the cell electrode stack is fully saturated with acid, the oxygen recombination proceeds very slowly. The rate of sulfation process also depends on the solubility of oxygen in sulfuric acid. However, in batteries that are stored with limited acid volume, oxygen can recombine rapidly. A small leak in the cell container results in rapid self-discharge of the negative electrode by the atmospheric oxygen. Hydrogen recombination at the positive electrode has been reported to be insignificant [12,13]. Primarily, only the negative electrode loses capacity, but when battery is recharged the positive electrode has to be overcharged with the same amount of charge, which has been already lost at the negative electrode through self-discharging process. This overcharge results in an equivalent loss of oxygen [9].

The rates of the other self-discharge reactions are primarily determined by the acid concentration [4,8]. High acid concentrations accelerate the gas evolution reactions at both electrodes [3,14]. In contrast, grid corrosion appears to be faster at low acid concentrations and voltages. Although corrosion of the grid material represents a slow self-discharge reaction [9,14,15]:

$$2H^+ + Pb + PbO_2 + 2HSO_4^- \rightarrow 2PbSO_4 + 2H_2O \tag{6}$$

Sulfation of unconverted lead oxide is so rapid that it generally occurs before the battery is shipped from the factory. Sulfation of PbO (in new cells) reaction is [14]:

$$H^+ + PbO + HSO_4^- \rightarrow PbSO_4 + 2H_2O \tag{7}$$

Batteries are sometimes recharged just before shipment to complete the conversion of lead oxide to lead dioxide in the positive plate. Although the self-discharging process is unavoidable, but it can be largely suppressed by addition of appropriate additives into the battery solution. The beneficial effect of different concentration of boric acid as an additive to sulfuric acid solution on the performance of positive electrode in lead-acid battery was reported by Badawy and El-Egamy [16] using linear sweep voltammetry, constant potential and impedance measurements. They proposed that the presence of boric acid modifies the PbO_2 deposit. Boric acid inhibits the formation of insulating $PbSO_4$ phase, and hence, decreases the self-discharge of formed PbO_2. The effect of different concentration of citric acid as an additive to sulfuric acid solution on electrochemical behavior of positive electrode (in PbO_2) and the negative electrode of a lead-acid battery was investigated by Wie and Wang employing voltammetry technique [17]. They reported formation of a new PbO_2 layer on positive electrode at the presence of citric acid. This layer is difficult to be reduced and this will be beneficial to the operation of lead-acid battery. The peak current associated with the formation and reduction of PbO_2 and with evolution of oxygen increases with the increase in concentration of citric acid. The limits of these effects are reached at a citric acid concentration of 2 g l^{-1} in 4.5 M H_2SO_4 solution. For the behavior of lead as a negative electrode, the peak current attributed to the oxidation of lead to $PbSO_4$ and the evolution of hydrogen gas also increase with the concentration of citric acid with the limits of these effects are reached at the concentration of 2 and 3 g l^{-1} citric acid in 4.5 M H_2SO_4 solution.

In this work, the effects of four different additives in electrolyte of AGM batteries on self-discharge have been investigated. The additives added to battery solution were sodium sulfate, boric acid, citric acid, and stearic acid with specific concentration.

2. Experimental procedure

The self-discharge of four AGM batteries containing additive in electrolyte was measured. The theoretical capacity of employed AGM batteries was 7 Ah. Since the open-circuit voltage (OCV) of the battery depends on the state of the charge a fully charged batteries at a constant voltage of 14.6 V were used throughout this investigation. The open-circuit voltage between anode and cathode was measured by Hioki Digital Hitester 3256-51 multimeter over 48 days at ambient. Reading was carried out every 4 days, and then the difference of measured OCV with the OCV measured on next 4 days was calculated as follow:

$$\Delta OCV = (OCV)_t - (OCV)_{t+4} \tag{8}$$

where $(OCV)_t$ and $(OCV)_{t+4}$ are the reading at the day of measurement and the reading that was measured on the next 4 days.

Five different battery electrolytes with the following concentrations were employed in this study.

Battery no.	Electrolyte composition
1	35% (w/w) H_2SO_4
2	35% (w/w) H_2SO_4 + 7.1, 9.94, and 21.3 g l^{-1} Na_2SO_4
3	36% (w/w) H_2SO_4 + 4 g l^{-1} boric acid
4	35% (w/w) H_2SO_4 + 3 g l^{-1} citric acid
5	35% (w/w) H_2SO_4 + 0.7 and 1 g l^{-1} stearic acid

In order to select the appropriate concentration of Na_2SO_4 additive in battery number 1, the capacity of each battery for discharge capability was measured. Each battery was fully charged with a constant voltage (14.6 V) by a charger, and then was discharged continuously with a constant current of 1 A until the battery voltage dropped to 10 V. All the electrolytes were prepared using analytical grade of appropriate chemicals and deionized water.

3. Results and discussion

The effect of different additives namely sodium sulfate, boric acid, citric acid, and stearic acid on self-discharge is discussed separately.

3.1. Sodium sulfate

Fig. 1 presents the variation of battery OCV with time for different concentration of Na_2SO_4 additive. It is evident that the initiation of self-discharge is affected by addition of Na_2SO_4 and increases as the concentration of Na_2SO_4 increases in the solution, although the rate of self-discharge is not affected by the concentration of Na_2SO_4. The rate of self-discharge for the first 4 days for all concentration is about 0.03 V day^{-1} and decreases to 0.01 V day^{-1} for the next days identical to the battery no. 1 that has no additives. In order to select the proper concentration of Na_2SO_4,the discharge capability of fully charged batteries with different concentration of Na_2SO_4 under a constant current of 1 A was measured and the values of 4.7 Ah for battery no. 2 (1), 5.1 Ah for battery no. 2 (2), and 5.05 Ah for battery no. 2 (3) was measured. Sodium sulfate salt has high solubility in water. The ions ${SO_4}^{2-}$ increase self-discharge in two ways. Firstly, at the presence of ions ${SO_4}^{2-}$ in electrolyte the following equilibrium proceeds to form ${HSO_4}^-$ ions:

$$ {SO_4}^{2-} + H^+ \Leftrightarrow {HSO_4}^- \qquad (9) $$

Increasing the concentration of ${HSO_4}^-$ ions in the electrolyte causes oxygen and hydrogen evolution and an increase on self-discharge reactions. Secondly, sulfate ions may also react with Pb^{2+} ions in electrolyte and form barrier layer of $PbSO_4$ on the electrode surface. These two processes cause an increasing on the battery self-discharge. On the other hand, formation of barrier layer of $PbSO_4$ causes a decrease in the conductivity of the electrode and results on the reduction of battery OCV especially during the first days.

3.2. Boric and citric acids

It is believed that PbO_2 film formed on electrode surface in the electrolyte containing boric acid to be thin, homogeneous, and adherent to the surface [16]. Under open-circuit conditions, the PbO_2 film formed in the presence of boric acid discharges at a slower rate leading to low total impedance. Once the outer lead dioxide layer has been discharged (this depends on the pre-anodization time), higher impedance is expected. This behavior is a proper indication that the presence of boric acid modifies the morphological structure of the PbO_2 crystals, which delays its self-discharge to $PbSO_4$ [16]. Since, the acidic constant of boric acid is very small ($pK_a = 9.24$) and it acts like a base rather than an acid, the concentration of sulfuric acid solution in electrolyte of battery no. 3 was selected grater than that of other batteries. Similar concentration of boric acid to work by Badawy and El-Egamy [16] was selected for the experiment. Readings of OCV measurements of battery no. 3 showed that the self-discharge has been decreased to 0.0025 V day^{-1} compared to the battery no. 1 (Fig. 2).

The addition of citric acid in electrolyte of battery affects on the self-discharge through two opposing factors. The adsorbed citric acid on the PbO_2 surface suppresses three-dimensional growth and accelerates the two-dimensional growth of PbO_2. This new layer of PbO_2 is more difficult to be reduced than that of PbO_2 produced in pure sulfuric acid [17]. Hence, it is expected that the amount of self-discharge in electrolyte containing citric acid to be smaller than that of battery without it. A concentration of 3 g l^{-1} similar to reference [17] was selected for this work. Fig. 2 shows the reduction of OCV of battery no. 4 is smaller than that of battery no. 1 during 48 days measurement. The rate of self-discharge for this battery is 0.0075 V day^{-1}. On the other hand, at the presence of citric acid decreases the overvolt-

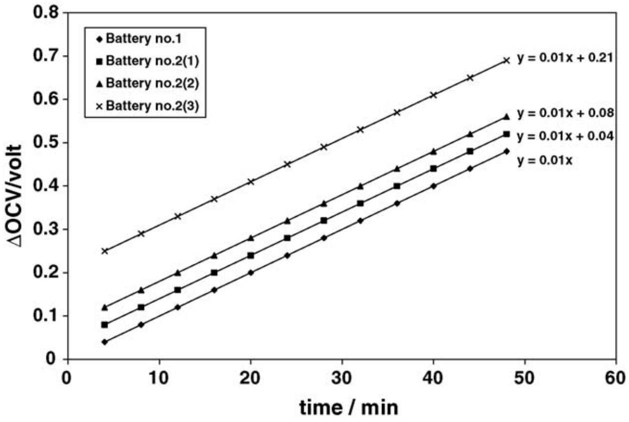

Fig. 1. Variation of OCV with time for battery nos. 1 and 2 containing 7.1 (1), 9.94 (2), and 21.3 g l^{-1} Na_2SO_4.

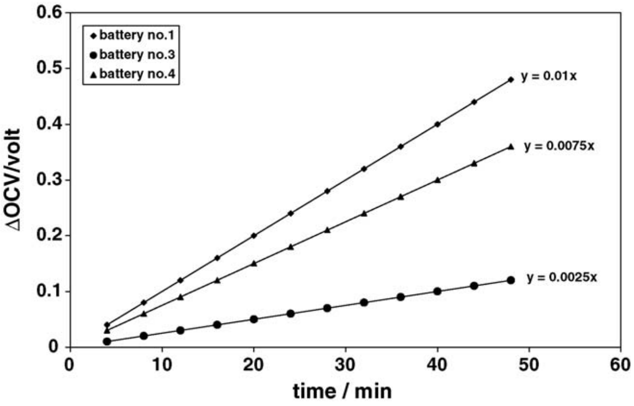

Fig. 2. Variation of OCV with time for battery no. 1 compared to batteries nos. 3 and 4.

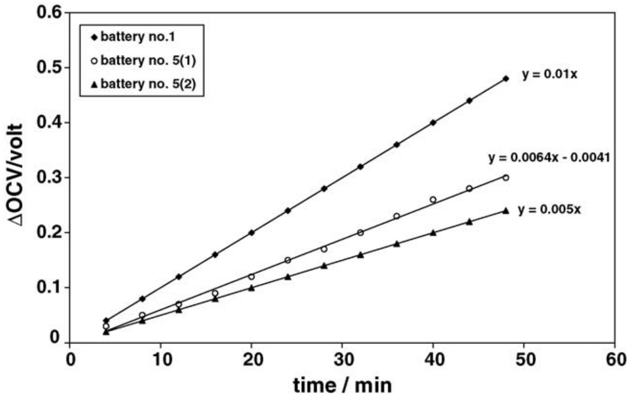

Fig. 3. Variation of OCV with time for battery nos. 1 and 5 containing 0.7 (1) and 1 g l^{-1} (2) concentrations of stearic acid.

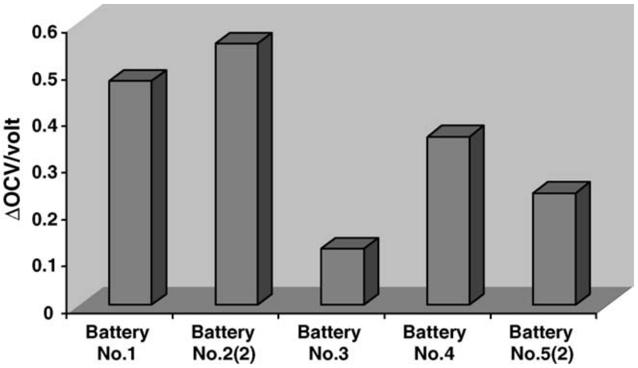

Fig. 4. The reduction of OCV for five selected batteries after 48 days.

age required for the oxygen and hydrogen evolution reactions [18], so may result on increasing battery self-discharge. The latter factor is opposite the former on the self-discharge process. It seems that the first factor prevails so the addition of citric acid in electrolyte decreases the self-discharge to some extent with respect to battery contains no citric acid. The formation and reduction of PbO_2 and evolution of oxygen increase with increasing the concentration of citric acid. The limits of these effects are reached at a concentration citric acid of 2 g l^{-1} in 4.5 M H_2SO_4. At the negative electrode, the oxidation of lead to $PbSO_4$ and the evolution of hydrogen both also increase with concentration of citric acid up to 2 and 3 g l^{-1}, respectively, but do not increase further with concentrations up to 6 g l^{-1} [17,18].

3.3. Stearic acid

Fig. 3 illustrates that the rate of self-discharge of battery containing 0.7 and 1 g l^{-1} stearic acid 35% by weight H_2SO_4 solution. The rate of self-discharge depends on the stearic acid concentration and increases with its concentration. The reduction on OCV for battery containing 0.7 g l^{-1} stearic acid after 48 days is 0.3 V while this reduction for 1 g l^{-1} concentration for the same period is 0.24 V. Since the solubility of stearic acid in sulfuric acid is negligible higher concentration of stearic acid was not selected. Stearic acid is a surface active agent that adsorbs on PbO_2 causes the three-dimensional growth of $PbO_2$to be inhibited and the two-dimensional growth to be enhanced similar to citric acid. This new layer of PbO_2 formed in presence of stearic acid is more difficult to be reduced than that produced from pure sulfuric acid. Citric and stearic acids have different effect on the rate of self-discharge because of their difference in the structures. Stearic acid is a surfactant that has a hydrophobic tail and a hydrophilic head but citric acid has four hydrophilic moieties. The molecules of stearic acid are only placed at the electrolyte–electrode interfaces and composed condensed monolayers which are coherent, rigid, and densely packed, with high surface viscosity. The molecules have little mobility and are oriented perpendicular to the surface. The condensed monolayers of stearic acid prevent from reaching of HSO_4^- ions to the surface of electrode, so the self-discharge reactions and oxygen–hydrogen evolution are decreased.

4. Conclusion

Boric and stearic acids are the effective additives for decreasing battery self-discharge. Boric acid and stearic acid decrease the rate of battery self-discharge from 0.01 to 0.0025 and to 0.005 V day^{-1}, respectively. Boric acid modifies the PbO_2 deposit without decreasing its formation efficiency from $PbSO_4$. Boric acid inhibits the formation of the insulating $PbSO_4$ phase, and hence, decreases the self-discharge of the formed PbO_2 [16]. Adsorption of stearic acid on PbO_2, and then formation of condensed monolayers of stearic acid at electrolyte-electrode interfaces decreases the rate of self-discharge to half of the rate of self-discharge of the battery without additives. Although the presence of citric acid in the electrolyte causes an increase on oxygen evolution reaction, but its adsorption on the lead and PbO_2 surfaces decreases the self-discharge to some extant. Presence of Na_2SO_4 additive speeds up the self-discharge process because of facilitating of formation $PbSO_4$ barrier layers and also increasing of HSO_4^- ion concentration. The effect of selected concentration of additives employed in this work on the reduction of open-circuit voltage during 48 days immersion is illustrated in Fig. 4. It is evident that the most effective additive was 1 g l^{-1} concentration of stearic acid with a reduction of 0.12 V on OCV after 48 days measuring.

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