A novel electrochemical approach on the effect of alloying elements on self-discharge and discharge delivered current density of Pb–Ca–Ag lead-acid battery plates

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ARTICLE INFO

ABSTRACT

The aim of this research is to examine the effect of alloying elements in positive plate composition of a lead-acid battery on its self-discharge and delivered current density in discharge state performances. To elucidate, a positive and negative lead-acid battery plates of two alloys namely Pb–Ca–Ag and Pb–Sb are investigated through electrochemical measurements in battery solution. Higher delivered current density of Pb–Ca–Ag cell in compare with Pb–Sb cell is observed for 25 days of 33 measurement days. The evolution of couple potential for both cases shows that the Pb–Ca–Ag cell potential achieves a value in the potential range of water stability after 25 days while in case of Pb–Sb cell, it remains well beyond the water stability potential domain for 33 days of measurements. Further investigations demonstrate that Pb–Sb cell current density is mainly caused by Pb oxidation reaction on negative plate while both anodic and cathodic polarizations (mixed polarization) are responsible in the case of Pb–Ca–Ag cell.

1. Introduction

During the past two decades, lead-acid batteries have been received too much consideration to modify grid manufacturing processes and chemical composition of the grid alloys in order to decrease battery grid weight as well as to reduce the production costs, and to increase the corrosion resistance and the battery life-time cycle. Furthermore, as the under hood temperature in new aerodynamically modified vehicles was increased, the service temperature of lead-acid batteries rose. The higher service temperature led to more rapid corrosion of positive grid and, consequently, resulted to rapid failure of such a battery [1–3].

Lead–calcium (Pb–Ca) based alloys were developed to bate these problems. Study on lead–calcium alloys was begun in early 1859, and the first application of these alloys in lead-acid batteries was reported in 1935. Lead–calcium alloys can improve the maintenance-free capability of lead-acid batteries due to high hydrogen evolution over potential. Minor alloying elements called as additives are, therefore, often used to improve the properties of lead–calcium alloys. In this alloying system, the common additive elements are tin and silver [2,4,5].

The influence of calcium, tin and silver content in these alloys has already been widely studied [1,4–9]. In tin containing alloys,

the tin content is sufficient to react with all the calcium in the alloy to produce Sn_3Ca, which has more strengthening effect than Pb_3Ca particles. Therefore, tin can improve mechanical properties of the alloy. These alloys have extremely corrosion-resistant surfaces, and battery grids produced from the alloys are considerably resistant to corrosion at elevated temperatures. This high corrosion resistance also promotes the adhesion between the grid and active material [1,4]. The effectiveness of tin to prevent the development of a high impedance passive layer at the grid active material interface has also been reported [6].

The newer alloys for start-lighting-ignition (SLI) batteries also contain silver which further reduces the rate of corrosion and makes the grids more resistant at elevated temperatures. It has been shown that silver had virtually no effect on the hydrogen evolution current. There was, however, a small increase in the rate of oxygen evolution when silver was present in the positive active material. Silver may enable the active material to conduct current even in a deeply discharged state, improving battery recharge ability [5,7–9].

Antimony can improve mechanical properties of lead alloy, cast ability and the adherence of active materials to the grid. It has been shown that antimony dopes the positive active materials during corrosion. The major problem of using antimony in grid alloy is its transfer to negative plate during cycling, where it increases the rate of gassing and, therefore, increases the water consumption [7,10–12]. It is believed that successive reduction of the antimony content in the grid alloys makes the

longer service intervals possible and reduces self-discharge rates [12–14].

The effect of self-discharge reactions on the shelf life of the lead-acid battery was first reported in 1882, which showed that the process of self-discharge happens gradually at room temperature [13]. It is claimed that with an increase in the temperature, the shelf life reduces considerably [16]. The self-discharge reactions are well defined and self-discharge rates in lead-acid batteries having immobilized electrolyte and limited acid volumes have been measured in several investigations [17–20]. From mechanistic point of view, the major contribution to self-discharge occurs at the negative electrode of a battery. Although comparable self-discharge reactions at the positive electrode exist, they are of minor importance because all substances that may reduce the oxygen overvoltage significantly are oxidized at the extremely positive potential. Hydrogen evolution reaction cannot be suppressed completely even at the open-circuit cell voltage [21].

The self-discharging process 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 using linear sweep voltammetry, constant potential and impedance measurements [22]. 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. They reported the 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 [23]. Similar findings on the effect of citric acid addition into battery solution was reported by Safari [24] and co-workers during their study on the effect of sodium sulfate, boric acid, citric acid, and stearic acid additives into battery solution on self discharge of an AGM batteries. They reported that although boric acid is the most effective additive on decreasing self-discharge, adsorption of citric acid on the lead and PbO_2 surfaces decreases the self-discharge to some extent [24].

Thus, the objective of the present work is to understand the effects of alloying elements in positive grid on self-discharge and current density delivery of the cell.

2. Experiments

Grids were produced using gravity casting process with different chemical compositions. Other processes such as lead oxide making, pasting, curing, electrical formation and electrolyte filling conditions were carried out according to the following specifications: positive paste density: 4.0–4.1 g cm^{-3}; lead free content in curing chamber: less than 2%; curing temperature range: 65–75 °C; crystal type for cured plate: 3 BS (basic sulfate), crystal type for positive formed plate: β·PbO_2, Chemical composition of negative and positive plates and associated paste compositions are shown in Table 1.

All electrochemical tests were carried out on finished plates of Pb–Ca–Ag and Pb–Sb grids. The plates used in this study were in their final stage of production which means the paste was applied on them and they were subjected to the formation procedure. Plates were cut into small slices with a surface area of 30 mm × 30 mm. Then an electrical connection was made by connecting a copper wire. An exposed area to the test solution of 400 mm^2 of the surface was prepared by masking the rest of the plate by beeswax–colophony blend. Mentioned blend is believed to have perfect adhesion and magnificent durability to test solution for long periods of time. Analytical grade solution of 4.88 molar H_2SO_4 and distilled water were used as acid battery solution throughout this work resembling the further work by Lambert et al. and Bullock et al. [25,26]. A strong acidic pH level of −0.250 was recorded for this solution at ambient temperature using calibrated pH meter. It should be noted that in case of short-term tests, fresh test solution was used for each case.

To study the electrochemical behavior of plates, three different tests were performed; two long term and a short term measurements. The self-discharging phenomenon with time passing for both positive and negative plates was evaluated by monitoring the open circuit potential respect to the saturated Ag/AgCl reference electrode of each plate. On this test, prepared plates according to described procedure were exposed to 500 ml test solution for 61 days. Rest potential of plates was measured every 48 h through a high input resistance electrometer connected to an ACM potentiostat (ACM instruments) for 300 s. The electrolyte level of test solution was kept at a constant level by addition of distilled water in order to remove the effect of two phenomena on the originality of the results; water evaporation or the risk of a change in solution concentration by means of adding fresh dilution. This test could help one to elucidate the effect of self-discharge on each single plate separately which could cause battery performance abatement.

A cell consists of a positive and negative plates was evaluated by measuring the couple current density between them and also measuring the associated cell voltage which was the purpose of second long term test. On this test, a negative and positive plate from each composition with the same surface area was connected to each other and then exposed to 500 ml test solution for 33 days. The couple potential and couple current density were measured for a period of 600 s every 96 h during 33 days of immersion in test solution. The aim of this test was to clarify the effect of self-discharge on battery performance in real practice since each cell could represent a minor battery.

In order to certify the observed electrochemical behavior of plate, in a three electrodes cell configuration consists of plate as working electrode, a saturated Ag/AgCl electrode as the reference electrode and 2 cm^2 of platinum foil as the counter electrode, potentiostatic polarization test was performed on both negative and positive plates of each alloy. Each plate was polarized by potentiostat device and the associated current density was measured (the difference between the rest potential of each plate and couple potential of the cell consisting negative and positive plates represents the amount of polarization in each case). All electrochemical measurements were performed at room temperature. It should be mentioned that all represented potentials are respected to saturated Ag/AgCl reference electrode. Also note that both platinum counter electrode and Ag/AgCl reference electrode were only maintained in the solution during the potential or current density measurements and then they were carefully pulled out to avoid solution contamination during long-term tests.

3. Results and discussion

3.1. Self discharge

As a crucial factor in battery performance, self-discharge phenomenon usually caused by sulfation can impose battery capacity reduction and even battery failure. Although water electrolysis process occurs mostly during charge/discharge cycle in a battery cell, it could also happen in open-circuit mode at lower rates. In many applications, batteries are subjected to relatively long periods of open-circuit mode waiting to be charged or discharged. In these

Table 1
Chemical composition of plates and their associated pastes.

Composition	Negative plate	Positive plate
Grid (Pb–Ca–Ag)	Pb–0.11%Ca–0.35%Sn–0.02Al (without Ag)	Pb-0.065%Ca-1.2%Sn-0.018Ag
Paste for Pb–Ca–Ag grid	Expander (barium sulfate–black carbon–sodium lignosulfonate)–stearic acid–sulfuric acid–water	Lead oxide powder–fiber flock–red lead–battery acid–water
Grid (Pb–Sb)	Pb-1.7%Sb-0.022%Se	Pb–1.7%Sb–0.022%Se
Paste for Pb–Sb grid	Expander (barium sulfate–black carbon–sodium lignosulfonate)–stearic acid–sulfuric acid–water	PbO powder–fiber flock–battery acid–water

cases water loss by "self-discharge electrolysis", consists of hydrogen evolution on the negative plates and oxygen evolution on the positive ones, may then represents an important part of total water loss in a battery cell [16,17].

Fig. 1A represents the result of rest potential measurements of positive plates of Pb–Ca–Ag and Pb–Sb for 61 days of immersion. At the first day of measurement, the recorded potential was about 1566 mV for both plates. From 5th day, potential of Pb–Ca–Ag positive plates began to decrease down to its minimum value of 1487.2 mV at the 27th day although after 28th day of measurement, potential gradually increased to its maximum value of around 1570 mV at the day of 60. However, the potential of Pb–Sb
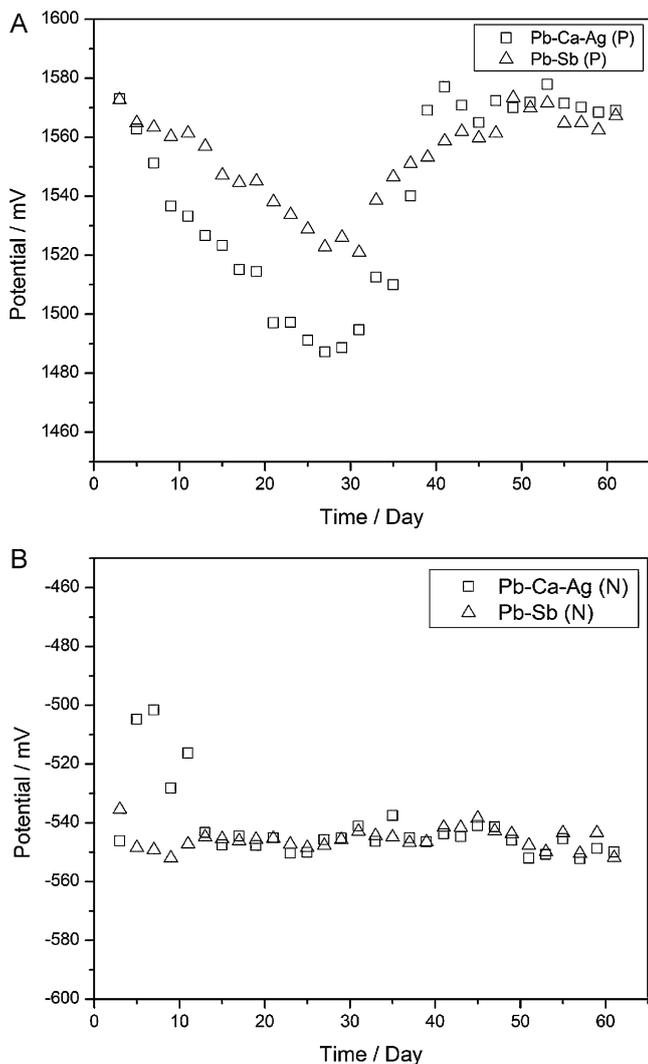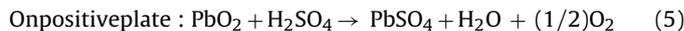

Fig. 1. Variation of rest potential during 61 days of measurement on: (A) positive plate of Pb–Sb and Pb–Ca–Ag alloys and (B) negative plate of Pb–Sb and Pb–Ca–Ag alloys.

positive plates exhibits reasonable stable condition in compare to the Pb–Ca–Ag plates. During 60 days of measurement its potential dropped from 1570 mV down to 1420 mV at 28th day of measurements and then began to increase to the final values of 1570 mV at the 60th day. Most probably, this decrease and increase in both cases is due to the employed method of plate preparation, i.e. cutting the plates in slices. Maybe, the positive grids are in contact with the solution, as a result of which conjugation reactions proceed between the grids and the PbO_2 active material and these processes continue until the grid surface is covered by a PbO_2 layer, i.e. the potential will decrease. When the whole grid surface is covered by the PbO_2 layer, the potential will start to increase and will reach a stationary value thereafter, which is actually observed in Fig. 1A. However, as shown in Fig. 1B the negative plates do not face this problem, as their active material is lead. The average potential values of positive plates in 60 days of measurement were 1542 and 1553 mV for Pb–Ca–Ag and Pb–Sb plates, respectively.

The result of rest potential measurements for negative plates of Pb–Ca–Ag and Pb–Sb is illustrated in Fig. 1B. The recorded value for the 1st day measurement seems to be in an unstable condition. From the 3rd day, a stable value of potential was recorded for negative plates. It is evident that the average measured potential for Pb–Sb negative plates has less fluctuation than that of Pb–Ca–Ag negative ones. The highest measured potential fluctuations of negative plates were 51.6 and 13.5 mV for Pb–Ca–Ag and Pb–Sb plates respectively. The negative plates potential fluctuations for both plates were similar during the test (see Fig. 1B). In other words, fluctuations were occurred in same days. For instance, between 25th and 29th days potential climbed and during 29th to 31st day's potential downfall was observed. The average values of negative plates potential in 61 days of measurement were −532 and −540 mV for Pb–Ca–Ag and Pb–Sb plates, respectively.

As shown in Fig. 2, the cell voltage, which is the potential difference between positive and negative plates, did not have noticeable fluctuations during 61 days long test and was around to 2100 mV.

According to the following electrochemical reactions, during self discharge, both positive and negative plates discharge spontaneously at their rest potential. For positive plate which is consisted of PbO_2, anodic and cathodic reactions (respectively) are:

$$H_2O \rightarrow 2H^+ + (1/2)O_2 + 2e^- \tag{1}$$

$$PbO_2 + 4H^+ + SO_4{}^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O \tag{2}$$

For negative plate which is consisted of Pb, following electrochemical reactions are known to be its anodic and cathodic reactions, respectively:

$$Pb + SO_4{}^{2-} \rightarrow PbSO_4 + 2e^- \tag{3}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{4}$$

The overall reactions on positive and negative plates are:

$$\text{On positive plate}: PbO_2 + H_2SO_4 \rightarrow PbSO_4 + H_2O + (1/2)O_2 \tag{5}$$

$$\text{On negative plate}: Pb + H_2SO_4 \rightarrow PbSO_4 + H_2 \tag{6}$$

Fig. 3. Mean values of couple potential vs. time plot for Pb–Ca–Ag and Pb–Sb alloys resulted from couple electrodes consisting negative and positive electrodes during 33 days measurements. The thermodynamic stability regions of H_2O, O_2 and H_2 have been shown by dashed lines.
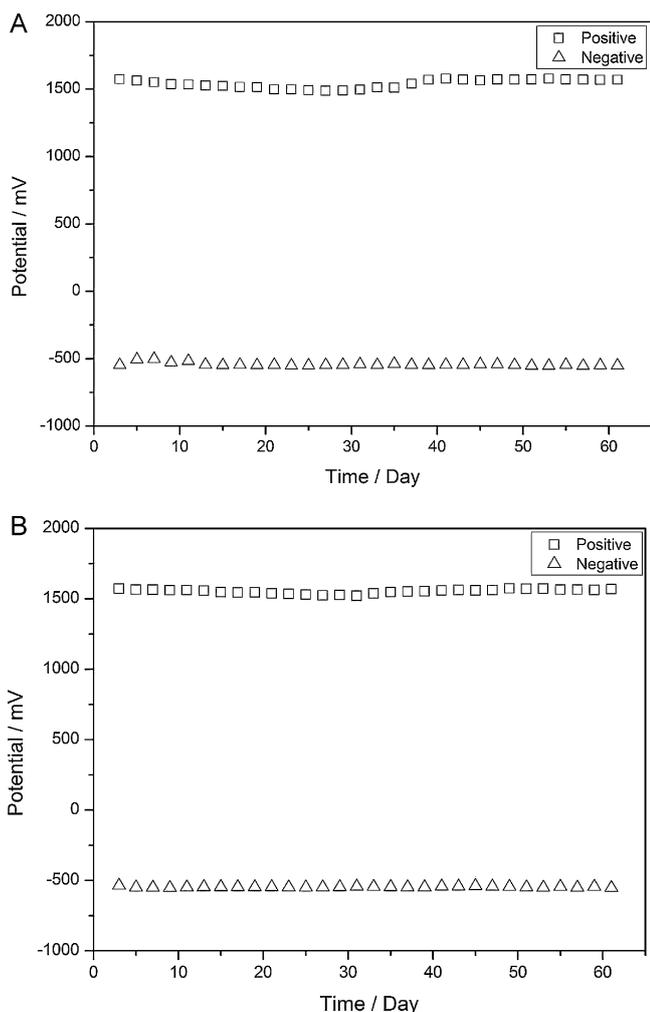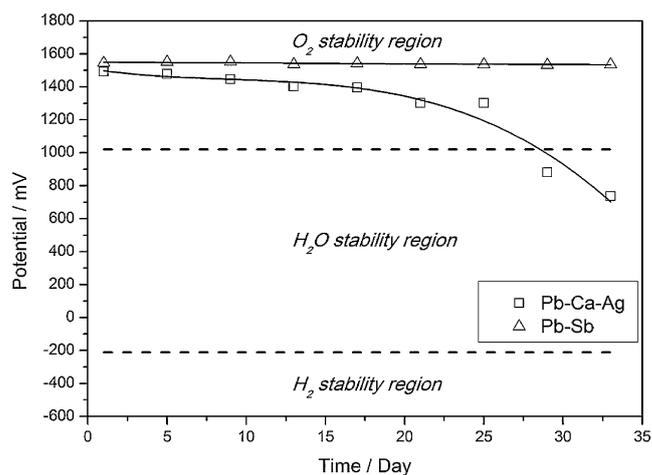

Fig. 2. Variation of rest potential with time for positive and negative plates of: (A) Pb–Ca–Ag and (B) Pb–Sb alloys during 61 days of measurement.

Therefore it will be obvious that sulfuric acid density decreases gradually over time. In other words, during self-discharge sulfuric acid is consumed and as a result the existence of $PbSO_4$ on both positive and negative plates with appearance of some water would occur. Although a slight devaition of around 30 mV and 50 mV from average value of open circuit potential for positive and negative plates is observed in Pb–Ca–Ag alloy case repectively (see Fig. 1), the diffrence in potential of negative and positive plates for both alloy remains around 2100 mV during 61 days of measurement, agreed by other researchers [15,27].

3.2. Current density delivery of cell

The delivered current density and couple potential of a cell constructed from a positive and negative plate for Pb–Ca–Ag and Pb–Sb alloys were measured through a zero resistance ammetry (ZRA) technique for 33 days. Fig. 3 shows the variation of couple potential for both Pb–Ca–Ag and Pb–Sb negative/positive couple plates with time. In case of Pb–Ca–Ag cell the couple potential drops in order of 755 mV from 1st to the final day of measurement (see Fig. 3). This drop consists of two different rates during the test period; sharp in first twenty days and then it slows down in last ten days. In contrast, for Pb–Sb case couple potential seems to be stable at around 1550 mV during 33 days. Although there is no sign of any considerable changes in couple potential of Pb–Sb cell during the course of measurement, this potential (~1550 mV) is very

close to the rest potential of Pb–Sb positive plate which indicates a massive polarization of negative plate. However, the couple potential for Pb–Ca–Ag case drops down noticeably after 20 days which implies the negative plate does not control the cell polarization solely. Hence, the cell exhibits a mixed polarization control which can be an advantage in battery performance.

After connecting Pb–Sb positive and negative plates to each other, negative plate acts like anode and polarizes severely anodic for about 2090 mV from rest potential of −540 mV to the average couple potential of 1550 mV according to electrochemical reaction (3), while positive plate polarizes slightly cathodic for about 3 mV from the rest potential of 1553 to average couple potential of 1550 based on cathodic electrochemical reaction of 2. The overall reaction of the cell, at which the cell voltage will be at couple potential status is:

$$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \qquad (7)$$
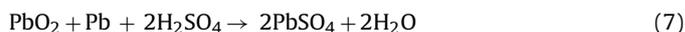
Taking into consideration a pH value of −0.250 for test solution and considering two main following electrochemical pH dependence reactions (electrochemical reactions (8) and (9)) that causes water loss in a battery solution, the potential region at which water is thermodynamically stable and beyond this region water is decomposed into hydrogen and oxygen gasses is illustrated in Fig. 3.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (8)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad (9)$$

An interesting observation is noticed that after 25 days and near 29th day from the beginning of the measurement, the cell voltage of Pb–Ca–Ag cell shifts from the region of water instability to stability region, while the cell voltage of Pb–Sb cell remains at the region of water instability for the 33 days of measurement. It is evident that the main reason of higher content of water loss in Pb–Sb cell is associated to higher polarization rate of negative plates rather than mixed control polarization that is obvious in Pb–Ca–Ag cell. Therefore, an antimony-free positive grid alloy, which in most cases is a positive lead–calcium–tin or lead–calcium–tin–silver alloy, is demanded by many automotive manufacturers, and represents the state-of-the-art for original equipment starter batteries with minimal water decomposition. Also, evolution of gasses and acid spilling are no longer critical issues [1,13].

The delivered current density of the cell associated to each cell is illustrated in Fig. 4. The average delivered current density for Pb–Ca–Ag cell begins from 0.224 mA cm^{-2} and then decreases
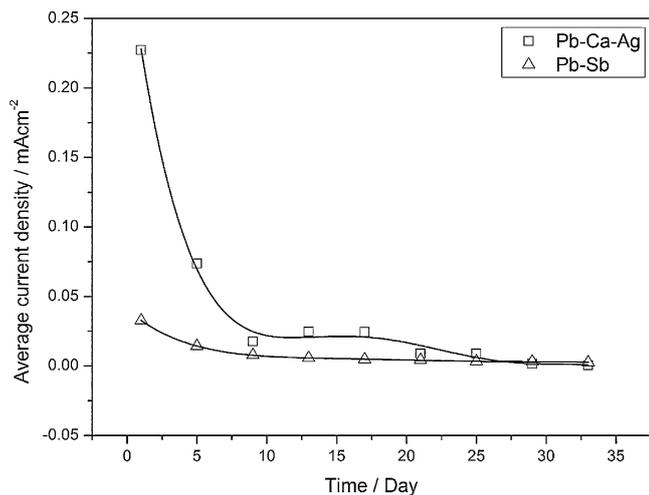
Fig. 4. Mean values of current density vs. time plot for Pb–Ca–Ag and Pb–Sb alloys resulted from couple electrodes consisting negative and positive electrodes during 33 days measurements.

gradually during the test and at the end of measurement (day 33) reaches to almost zero, whereas the delivered current density of Pb–Sb cell is considerably lower and it drops from the initial value of 0.035 mA cm^{-2} at the beginning of the measurement to almost zero after 12 days. The results of delivered current density of two cells also clearly demonstrate that Pb–Ca–Ag cell has a higher capacity for current output in compared to the Pb–Sb cell [8]. From the presented results, one can deduce that the high initial value of current density for Pb–Ca–Ag cell in contrast with low value of Pb–Sb cell (see Fig. 4) can be attributed to the cell polarization characteristics which is under mixed control of anodic and cathodic reactions for Pb–Ca–Ag cell while the response of the Pb–Sb plates on anodic and cathodic polarization was slow because of slow-footed reduction reaction rate of PbO$_2$ on positive plate.

3.3. Potentiostatic test

In order to simulate the reactions which are occurred on each plate via potentiostatic polarization, creating their natural polarization during couple to each other as happens in a battery, the average value of rest potential of each plate, the average cell voltage of each cell from previous experiments were selected as the base decision for applied constant potential. Table 2 illustrates the mean value of rest potential for negative and positive plates and also the mean value of measured couple potential of a cell consisting negative and positive plates. The difference between mean values of rest potential and couple potential shows the amount of mean magnitude of polarization which each plate experienced during connection to each other. Therefore, the positive plates of Pb–Ca–Ag and Pb–Sb are polarized cathodically for 105 and 12 mV, respectively. At the same time the negative plates of Pb–Ca–Ag and Pb–Sb are polarized anodically about 1782 and 2081 mV, respectively. The potentiostatic polarization of each plate was based on their polarization behavior during their discharging while couple to each other which means the positive plates of Pb–Ca–Ag and Pb–Sb were polarized 192 and 12 mV respect to their rest potential cathodically and the resulting cathodic current density was measured for 1200 s. Meanwhile, the negative plates of Pb–Ca–Ag and Pb–Sb were polarized 1782 and 2081 mV anodically respect to their rest potential and the resulting current density was measured 1200 s.

Figs. 5 and 6 illustrate the result of potentiostatic polarization behavior of negative and positive plates of each alloy respectively. The current density obtained from negative plates which are polarized anodically is illustrated in Fig. 5. As it is observed at the
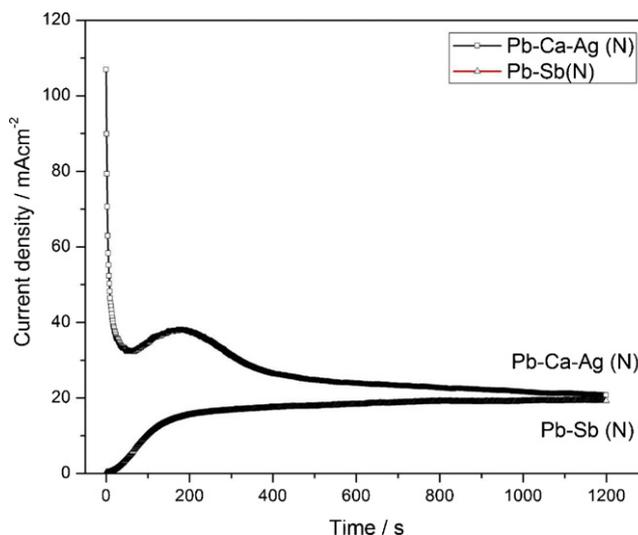

Fig. 5. Anodic current density vs. time plot for Pb–Ca–Ag and Pb–Sb negative plates at applied anodic potential of 1782 and 2081 mV, respectively.
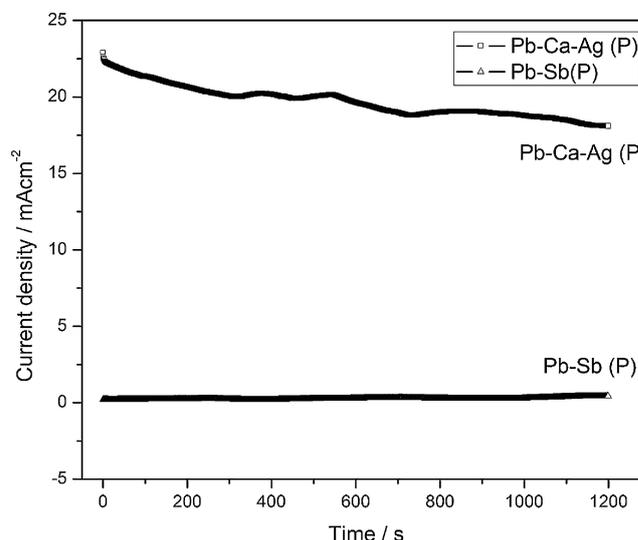

Fig. 6. Cathodic current density vs. time plot for Pb–Ca–Ag and Pb–Sb positive plates at applied cathodic potential of 292 and 12 mV, respectively.

beginning of test, the anodic current density for Pb–Ca–Ag negative plate begins from 109 mA cm^{-2} and then decreases to 33 mA cm^{-2} after 50 s of polarization. After a slight increase in anodic current density it further continues to decrease until reaches to a stable value of 20 mA cm^{-2} at the end of experiment. However, for Pb–Sb negative plate the measured anodic current density starts from zero and increases gradually to 20 mA cm^{-2} at the end of test. Thus, both the specimens reach almost a constant value of anodic current density at the end of the test. Considering the electrochemical reaction of positive plate during cathodic polarization a huge difference between alloys could be seen. The cathodic current density resulted from cathodic polarization of Pb–Ca–Ag positive plate begins from 22 mA cm^{-2} and after a gradual decrease reaches to 16 mA cm^{-2} at the end of the experiment. Whereas the response of positive plate of Pb–Sb alloy on cathodic polarization is somehow unpolarized behavior meaning its respond on cathodic polarization causes no appropriate cathodic current density. The measured current density begins almost at zero and after a slight increase, it reaches to a value around 2 mA cm^{-2} meaning almost 7 times less than Pb–Ca–Ag positive plate.

Table 2
The mean potential of plates in both rest and connected mode. The potentiostatic polarization value of each plate has been also calculated.

	Plate definition			
	Pb–Ca–Ag		Pb–Sb	
	Positive	Negative	Positive	Negative
Mean rest potential (mV)	1542	−532	1553	−540
Mean couple potential (mV)	1250		1541	
Amount of potentiostatic polarization (mV)	−292	1782	−12	2081

Comparing the almost near 22 mA cm^{-2} anodic current density of negative plate with 16 mA cm^{-2} cathodic current density of the positive plate for cell made from Pb–Ca–Ag alloy proves that the delivered cell current density is controlled by both electrochemical reactions that are taking place on positive and negative plates according to the PbO$_2$ reduction and Pb oxidation reactions (electrochemical reactions (2) and (3)). This state can be named as mixed controlled polarization. Whereas comparing the distinct anodic and cathodic current density of 22 and 2 mA cm^{-2} on negative and positive plates of Pb–Sb alloy, it could be inferred that the prepared delivered current density of cell during discharge is controlled by Pb oxidation reaction on negative plate according to the electrochemical reaction (3).

Taking into account that electrochemical response of negative and positive plates especially at the beginning of anodic and cathodic polarization (see Figs. 5 and 6) reveals that both negative and positive plates of Pb–Ca–Ag alloy responding much better in compare to the Pb–Sb plates to the polarization. Therefore Pb–Ca–Ag plates expected to perform better in conditions which high current density is needed, like at starting in automobiles.

4. Conclusions

1) The measurement of rest potential for both cases shows no severe fluctuations. The potential difference between negative and positive plates in each alloy remains constant around 2100 mV for 61 days of measurement.
2) The average couple potential for Pb–Sb cell remains near to the rest potential of positive plate, i.e. massive polarization of negative plate takes place which means the electrochemical process this cell is controlled by anodic reaction on negative plate during discharging. While, for Pb–Ca–Ag case the measured couple potential decreases considerably from near the positive plate rest potential to a median value between positive and negative plates. This expresses that the electrochemical process in Pb–Ca–Ag cell is controlled by mixed polarization of anode and cathode.
3) Pb–Ca–Ag cell potential reaches the water stability region after 25 days while for Pb–Sb cell, it remains well beyond the water stability potential domain for whole 33 days of measurements. This could enhance the battery performance by decreasing the water loss of battery electrolyte.
4) Potentiostatic polarizations in compliance with the couple current density measurements demonstrate that the cell current density is mainly caused by Pb oxidation reaction on negative plate for Pb–Sb cell while both anodic and cathodic polarizations are responsible in the case of Pb–Ca–Ag cell.
5) The higher initial value of cell current density as well as higher anodic and cathodic current density during potentiostatic polarization of Pb–Ca–Ag plates were compared with Pb–Sb ones can be attributed to the superior electrochemical response on Pb–Ca–Ag plates due to the mixed-polarization state while slow anodic and cathodic polarization of Pb–Sb plates could be the result of slow-footed reduction reaction rate of PbO$_2$ on positive plate.

Acknowledgements

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