



Short communication

Influence of the active mass particle suspension in electrolyte upon corrosion of negative electrode of a lead-acid battery



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HIGHLIGHTS

- We studied the influence of the particles of positive active mass suspension.
- Considerable increase of the Pb-electrode corrosion at the contact of slime particles.
- The appearance mechanism macro-defects on lugs of the negative plates is offered.

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ABSTRACT

The influence of the suspension of positive active mass particles in the electrolyte on the performance of the negative electrode in a lead-acid battery is studied. A significant increase in the rate of corrosion of the lead electrode is shown when slime particles get in contact with its surface, which may result in the rise of macro-defects on the lugs of the negative electrodes.

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1. Introduction

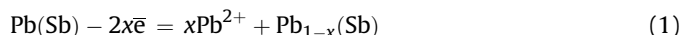
There has been a great of research on the corrosion of positive electrodes in lead-acid batteries [1–3], but the common perception is that negative electrodes would not corrode because such electrodes involve a reduction reaction. There are reports showing that negative electrodes corrode under special circumstances [4–8].

This is accounted for by the fact that the corrosive decay of the negative grid lugs is one of the most frequent causes of failures of lead-acid batteries. The corrosive process taking place on the negative grids under cathodic protection arises when electrolyte fills thin gaps where straps are cast onto the grid lugs. Omae et al. [4] hypothesized that local corrosion processes develop in such gaps due to a shift of potential in the positive direction along the gap. The rate of this corrosion may be up to 0.4–0.5 mm/year at 20 °C, and it grows as the temperature rises [4]. The corrosion

products have a greater specific volume than that of the initial lead, and it creates mechanical breaking force which affects lugs and strap interface.

It is possible to prevent corrosive and mechanical decay of the lugs/strap joint by selecting correct casting-on temperatures and compositions of alloys that lugs and strap are made of, thereby providing a positive meniscus without gaps in the cast-on joints [6].

One more cause of corrosion of negative grids made of Pb–Sb alloy is the contact corrosion, which is another type of local corrosion. The structure of Pb–Sb alloy consists of a solid solution of antimony in lead, eutectic, and phase inclusions of antimony which appear because of dissociation of the oversaturated solid solution during its cooling. Therefore, the alloy surface is rather uniformly covered with short-circuited galvanic cells. Under these circumstances, lead basically undergoes oxidation:



while on antimony the process of reduction of hydrogen takes place:

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Since the overpotential of hydrogen evolution on antimony is rather moderate, the rate of reaction (2) rate will be substantial. On the Pb/Sb contact point a steady potential is formed, being positive with respect to the equilibrium potential of lead and being negative with respect to the equilibrium potential of antimony. As the distance from the contact point increases, the potential will be shifting to the negative into the depth of lead, and at a certain distance it will reach the equilibrium potential of this metal. As to antimony, the further inside it, the more the potential will be shifting to the positive, converging to the equilibrium potential of this metal. The distance at which the changes of potentials take place depends on the electrical conductivity of the electrolyte. In a discharged battery when the electrical conductivity of acid is low, the area of contact corrosion is small, whereas in a charged battery it spreads to noticeable distance. In order to preclude the development of contact corrosion, alloys with a low content of Sb or Pb–Ca are being used in modern lead-acid batteries.

When a lead-acid battery is being used, its charged positive active mass (PAM) consisting mainly of PbO_2 , may partially shed fine particles of lead dioxide (FPLD) which may further be carried to the negative grid by the flow of the electrolyte. This process should be most noticeable in batteries with agitated electrolyte. ‘Bubbling’ and ‘Airlift’ agitation systems used nowadays have been described in paper [9]. Agitating creates electrolyte flows capable of carrying FPLD from the positive electrode to the lugs of the negative electrode. FPLD can have either temporary short-term contact with the lugs of the negative electrode, or they can get fixed thereon in rough places, pits or cracks. In any case, the contact of PbO_2 particles with the lugs of the negative grid creates appropriate conditions for the development of contact corrosion of the negative electrode lugs.

The effect of FPLD on the rate of corrosion of the negative electrode lugs is studied in this paper.

2. Experimental

The electrode made as a rectangular strap of pure lead was placed into a sulphuric acid solution (4.87 mol l^{-1}). The surface of the electrode had been previously cleaned and polished. The

electrode potential was measured in three conditions: 1) in non-agitated electrolyte; 2) in agitated electrolyte; 3) in agitated electrolyte with FPLD suspension.

FPLD was added into the electrolyte on the basis of 40 g l^{-1} . The slime assay showed that it contained 91–92% PbO_2 and 6–7% PbSO_4 . The temperature in the cell was maintained at 20°C . The duration of measurement of potential was 24 h.

The corrosion tests of lead electrodes were carried out in the following modes.

Mode 1 (reference mode). Corrosion test of a lead electrode in $4.87 \text{ mol l}^{-1} \text{H}_2\text{SO}_4$. Duration of testing was 340 h; at a normal room temperature. The weight of the electrode was 32.058 g, the total surface was 7.52 cm^2 .

Mode 2 (simulation of functioning of the negative grid with FPLD fixed on its surface). The surface of the lead electrode was covered with FPLD. To ensure reliable fixing, the electrode was wrapped with a layer of AGM separator on top. The resulting construction was placed horizontally into a solution of $4.87 \text{ mol l}^{-1} \text{H}_2\text{SO}_4$. Corrosion tests continued for 340 h. The weight of the electrode was 33.623 g; the total surface was 8.74 cm^2 .

Mode 3 (simulation of functioning of the negative grid in the flow of electrolyte with FPLD suspension). Corrosion testing of the lead electrode was carried out in agitated electrolyte with FPLD suspension. FPLD content in electrolyte was 40 g l^{-1} . Agitation continued for 48 h. The weight of the electrode was 73.051 g; the total surface was 17.05 cm^2 .

After testing, all the samples were washed in alkaline solution with an addition of sugar to remove the corrosive film, and the loss of electrode weight was determined. FPLD were analysed for the content of PbO_2 and PbSO_4 .

3. Results and discussion

Fig. 1 shows the variation of potential of the lead electrode in sulphuric acid solution in the non-agitated and in the agitated electrolytes, and also in the agitated electrolyte with FPLD suspension. It can be seen from the figure that the potential of the lead electrode in the non-agitated electrolyte steadily retains the value at about -0.305 V (hereinafter the potential values are given in regard to the normal hydrogen electrode). After being kept in the non-agitated acid for 24 h, the potential of the lead electrode was 0.304 V .

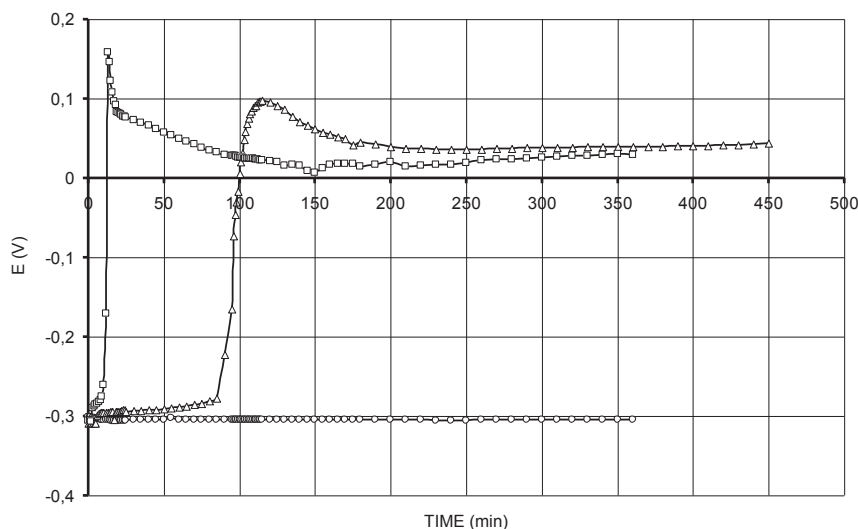


Fig. 1. The potential of the lead electrode during its retention in electrolyte. Testing modes: 1) electrode kept in non-agitated electrolyte (\circ), 2) electrode kept in agitated electrolyte (\triangle), 3) electrode kept in agitated electrolyte with FPLD suspension (40 g l^{-1}) (\square).

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