

Negative corrosion of lead–antimony alloys in lead–acid batteries at high temperatures

Takao Omae ^{*}, Shigeharu Osumi, Katsuhiko Takahashi, Masaharu Tsubota

Corporate R&D Center, Japan Storage Battery Co., Ltd., Nishinosho, Kisshoin, Minami-ku, Kyoto 601, Japan

Received 19 November 1996; accepted 30 November 1996

Abstract

When lead–acid batteries are used at high temperatures, corrosion is sometimes observed in negative components made of lead–antimony alloys. This corrosion seems to be caused by the antimony contained in lead alloys. We examined the effects of temperature, the concentration of sulfuric acid, and the configuration of test specimens on negative electrode corrosion. We also explored the mechanism by which negative component corrosion occurs when using lead–antimony alloys. Specimens in the electrolyte were not corroded at all, but portions just above electrolyte level and inside tiny spaces were corroded. The reason for this corrosion seems to be as follows. Corroded areas are covered with an electrolyte film that has a high resistance, so they cannot be polarized to the full cathodic protection potential. However, as lead–antimony alloys have a dendritic microstructure, with metallic antimony dispersed throughout the lead phase, local cell reactions between Sb and Pb occur in corroding areas, resulting in the evolution of hydrogen gas and the formation of lead sulfate.

Keywords: Lead–acid secondary batteries/general; Lead battery plates

1. Introduction

There has been a great deal 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, but there are as yet few instances of such research [4,5].

This paper reports on the results of our investigation concerning the effects of various factors on the corrosion of negative electrodes in flooded lead–acid batteries, and the corrosion mechanism.

2. Experimental

2.1. Effects of various factors on the corrosion of negative electrodes

Table 1 shows the purposes and the methods of the tests. Using the negative electrode as the test electrode and the

^{*} Corresponding author.

Table 1
Description of tests. Electrode alloys: A = Pb–4%Sb; B = Pb–0.1%Ca; C = pure Pb

Purpose	Electrode alloy	Electrolyte	Remarks
1 Effects of test electrode alloy	test electrode: A, B counter electrode: C	90°C, s.g. = 1.40	
2 Effects of counter electrode alloy	test electrode: B counter electrode: A, C	90°C, s.g. = 1.40	
3 Effects of electrolyte temperature	test electrode: A counter electrode: C	25, 50, 75, 90°C s.g. = 1.40	
4 Effects of electrolyte concentration	test electrode: A counter electrode: C	90°C s.g. = 1.05, 1, 10, 1.20, 1.30, 1.40	
5 Effects of gas atmosphere	test electrode: A counter electrode: C	90°C, s.g. = 1.40	bubbled H ₂ and O ₂ gas around test electrode; used H-type cells

positive electrode as the counter electrode, we supplied a constant current and, after the test, checked the extent of corrosion that had occurred on the test electrode (that is, the extent to which the electrode thickness had decreased). In all tests we set the current density to 30 mA cm^{-2} in that part of the electrode that was submerged in the electrolyte.

Fig. 1 shows the cell used for tests 1–4. The submerged portions of the test electrodes were wound in microfiber glass mat. This was done to maintain a constant electrolyte level around the test electrodes because corrosion occurs on those exposed parts of the electrodes that are slightly above the electrolyte level. In the fifth test we put the test electrode and counter electrode in an H-type cell (Fig. 2) to isolate them from one another and supplied a current while bubbling H_2 or O_2 around the test electrode. The gas-flow rate was set at 50 ml min^{-1} .

2.2. Effects of electrode configuration

While negative electrode corrosion occurs on an electrode's exposed portion, it is possible that, depending on the electrode configuration, it also occurs on the submerged portion, so we studied the effects caused within tiny spaces. The test electrode alloy was in all cases Pb–4% Sb, and the counter electrode was pure Pb.

We varied the sizes of the spaces from 0.05 to 5.0 mm in electrodes with shallow spaces (type A) and in electrodes with tunnel-like spaces that pass all the way through the material (type B); see Fig. 3. We supplied a current to the

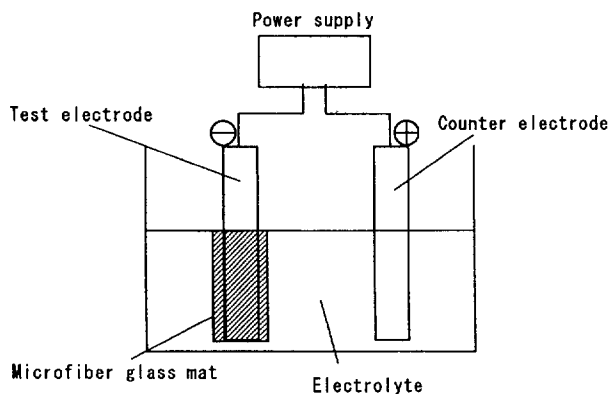


Fig. 1. Schematic diagram of the experimental cell.

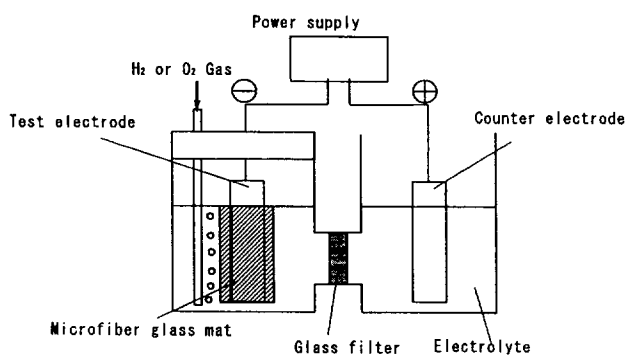
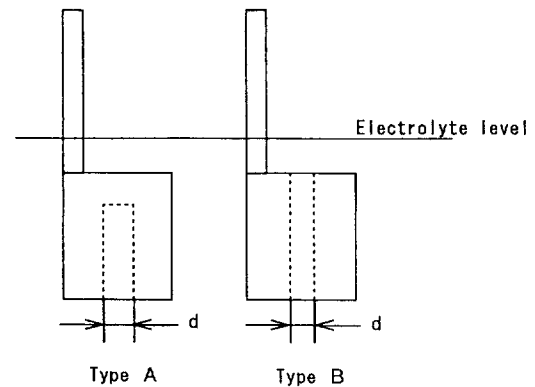


Fig. 2. Schematic diagram of the H-type cell.



$d=0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 \text{ (mm)}$

Fig. 3. Locations and dimensions of spaces within the test electrodes.

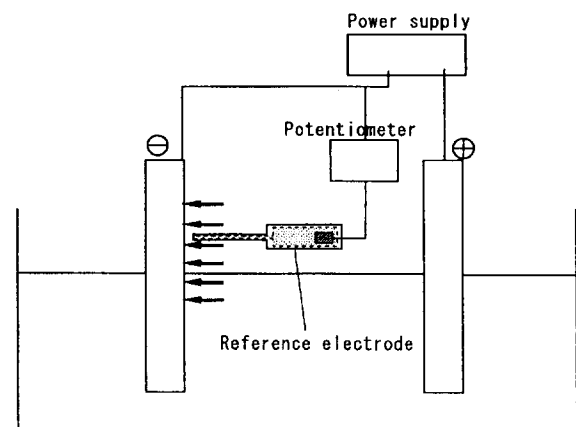


Fig. 4. Schematic diagram of the experimental cell used for measuring the electrode potential.

negative electrodes, which were submerged in electrolyte, and checked the post-test state of corrosion.

2.3. Potential of corroded portions

Fig. 4 shows the cell for measuring the potential within corroded portions.

A Pb/PbSO₄ electrode (in s.g. = 1.28 sulfuric acid gel) with a tip about 1 mm in diameter was used as the reference electrode. Electrical potential distribution was measured vertically by bringing the reference electrode's tip in contact with the submerged and exposed portions of the test electrodes.

3. Results and discussion

3.1. Effects of test electrode and counter electrode alloy

Fig. 5 shows cross-sectional photographs of test electrodes after testing. When testing the Pb–4%Sb alloy test electrode and the pure Pb counter electrode we found corrosion on the test electrode. On the other hand, with the Pb–0.1%Ca alloy test electrode and the pure Pb counter electrode, no corrosion

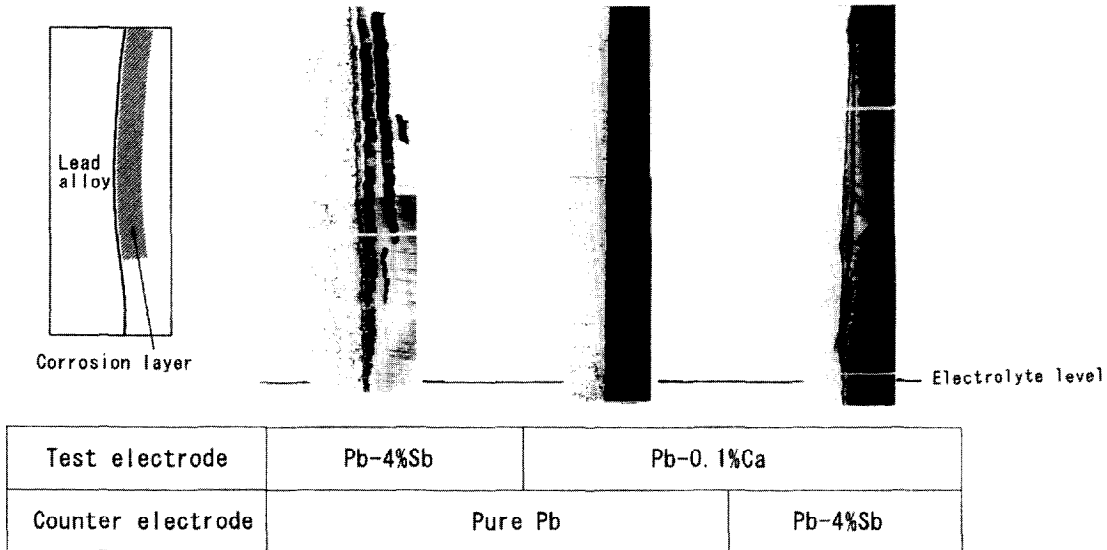


Fig. 5. Cross-sectional appearance of test electrodes after corrosion test.

was discerned, but corrosion occurred when using the Pb-4%Sb alloy for the counter electrode. This suggested that Sb is involved in negative electrode corrosion. It seems the reason for corrosion occurring when Pb-Sb alloys are used in the counter electrode is that Sb dissolving out of the counter electrode is electrodeposited on the negative electrodes.

3.2. Effects of electrolyte temperature

We examined the cross sections of test electrodes after supplying a constant current for 10 days, and measured the extent to which corrosion had reduced the thickness of the parent material (corrosion depth). Fig. 6 shows the relation between test temperature and corrosion depth. There was very little corrosion at temperatures below about 50°C, but when the temperature rose above 60°C, corrosion proceeded rapidly.

3.3. Effects of electrolyte concentration

Fig. 7 shows the relation between electrolyte specific gravity and corrosion depth. As specific gravity increased, corrosion depth increased.

j41

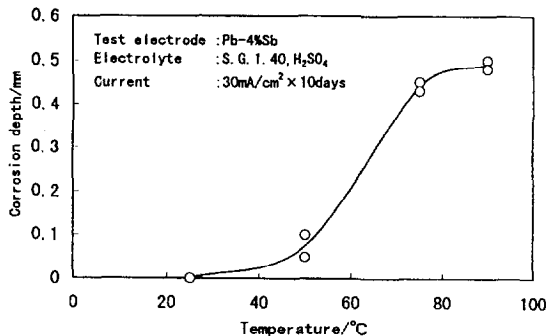


Fig. 6. Relationship between temperature and depth of corrosion.

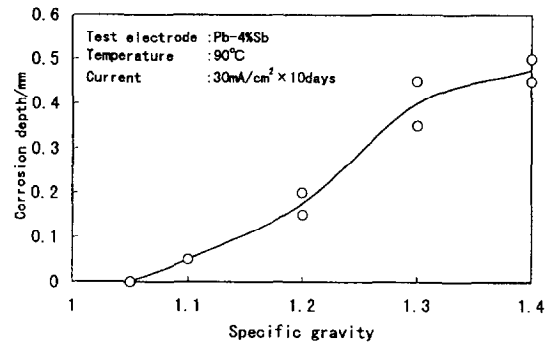


Fig. 7. Relationship between specific gravity and depth of corrosion.

3.4. Effects of atmospheric gas

We measured corrosion depth on the test electrode after supplying constant current for 10 days in an atmosphere of either H₂ or O₂. We discerned no difference in corrosion depth for, with either gas, the depth was about 0.48 mm. This suggested that the gas itself is not involved in corrosion, but that instead it indirectly results in corrosion by exposing the test material.

3.5. Effects of electrode configuration

Fig. 8 shows photographs of electrode cross sections taken after corrosion testing, and Table 2 shows the test results. Corrosion occurred in all the samples with shallow spaces, and in the samples with tunnel-like spaces of under 0.2 mm. This is an indication of how easily gas can accumulate inside the spaces. If gas accumulates inside spaces, then submerged portions exposed to the gas will corrode in the same way as portions exposed above the electrolyte level. Corrosion is therefore perhaps caused by the same mechanism. Because the gas accumulating in the spaces is likely to be H₂, this would corroborate the observation in Section 3.4 that the composition of the gas is not involved in the corrosion.

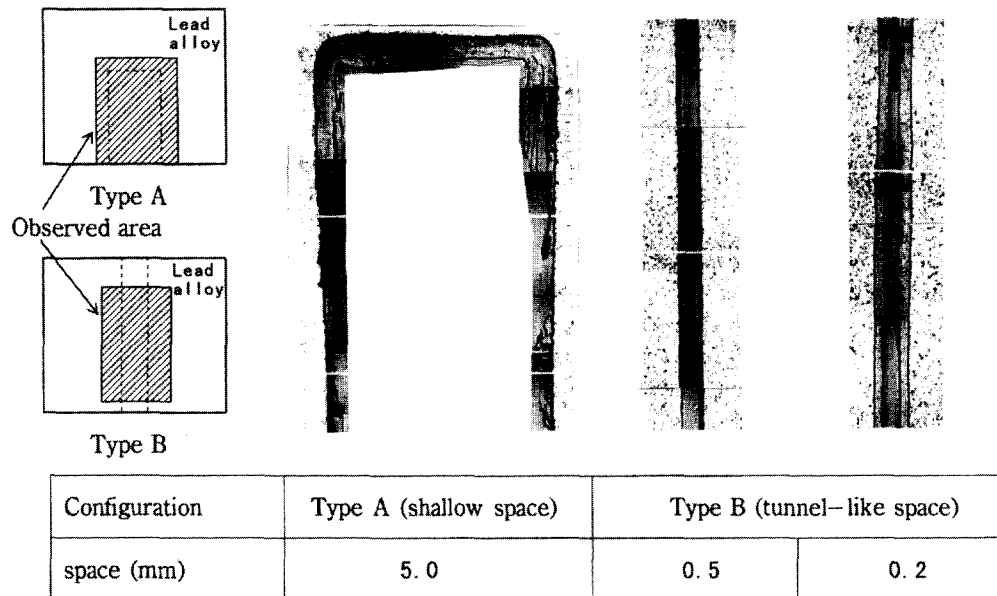


Fig. 8. Cross-sectional appearance of test electrodes containing spaces after corrosion test.

Table 2
Effects of spaces on the corrosion of negative electrodes

	Spaces (mm)						
	0.05	0.1	0.2	0.5	1.0	2.0	5.0
Type A (shallow space)	O	O	O	O	O	O	O
Type B (tunnel-like space)	O	O	O	X	X	X	X

O = corroded; X = not corroded.

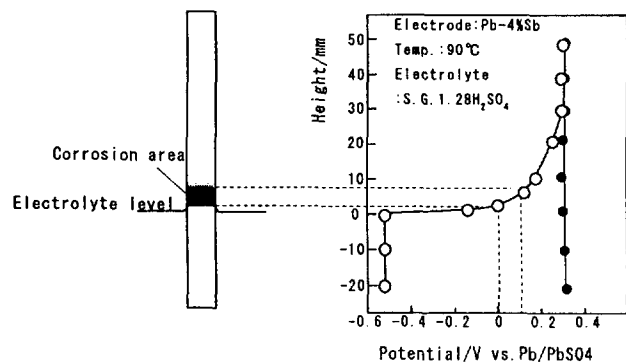


Fig. 9. Potential distribution on the negative electrode. O = current of 10 mA cm^{-2} ; ● = zero current.

3.6. Potential of corroded portions

Fig. 9 shows the results of potential distribution measurements. Both submerged and exposed places have the same potential in the absence of an electrical current, i.e. the open-circuit potential of the Pb–4%Sb alloy.

When a current was supplied, the surface of the submerged portion polarized until reaching the hydrogen-evolving potential. As the reference electrode was moved upward from the electrolyte level, the potential gradually approached the

open-circuit potential of the Pb–4%Sb alloy. The potential of the area where corrosion occurred was near to the Pb/PbSO₄ equilibrium potential. We assume that variation in potential occurs above the electrolyte level because of the *IR* drop in the thin layer of electrolyte on the electrode's surface.

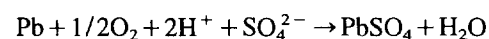
Similar electrical potential measurements of portions exposed above electrolyte level have been made by Pavlov et al., for Pb–Sn alloy plates through which a current had been supplied to the negative side [5], and by Wagner, for negative copper plates in lead–acid batteries [6].

As in our tests, these researchers reported that the *IR* drop in the thin layer of electrolyte on exposed portions brought about a gradual positive shift in potential as location proceeded upward from the electrolyte level.

4. Negative electrode corrosion mechanism

4.1. Corrosion mechanism

It is known that negative electrode corrosion in valve-regulated lead–acid batteries is caused by oxygen reduction [5], as shown in the following equation. In the experiments described here we therefore proceeded initially under the assumption that oxygen reduction is responsible for corrosion of Pb–Sb alloys.



But, as our test results showed no difference in the extent of corrosion whether the atmosphere was oxygen or hydrogen, this implied that corrosion in Pb–Sb alloys caused by oxygen reduction is very slow. We therefore conceived the mechanism shown in Fig. 10. The structure of Pb–Sb alloys is such that the Pb phase (α phase) and Sb phase (β phase) are mixed, and even when Sb is electrodeposited over a Pb–

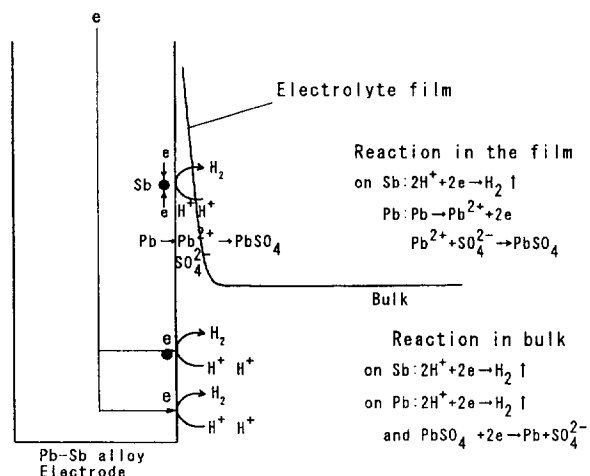


Fig. 10. Mechanism of corrosion of Pb-Sb alloys at negative electrodes.

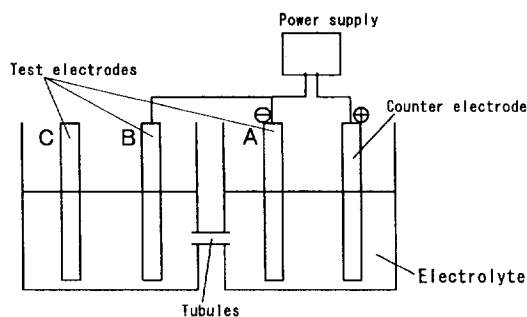
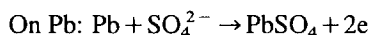
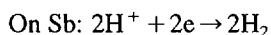


Fig. 11. Schematic diagram of experimental cell used to explore the corrosion mechanism.

Ca alloy the Sb is dispersed over the alloy's surface. The places where corrosion occurs are only slightly wet with a thin layer of electrolyte, and it would seem that this thin layer is responsible for the high resistance. When submerged electrode areas polarize to the point where hydrogen evolves, the corroding parts approach the Pb/PbSO₄ equilibrium potential. At this potential, hydrogen evolves on Sb, and Pb is not sufficiently polarized to the cathodic protection potential, so the electrons supplied on account of the hydrogen evolution on Sb are supplied by Pb, which changes to PbSO₄.



The causes of corrosion are therefore the hydrogen evolution reaction that occurs on Sb and the dissolution of Pb. The reason that corrosion is accelerated under high temperatures and high sulfuric acid concentrations seems to be that

the hydrogen overpotential on Sb declines, which leads to increased hydrogen evolution.

4.2. An experiment to demonstrate the corrosion mechanism

We performed the following experiment to demonstrate the mechanism described in Section 4.1, using the test cell shown in Fig. 11. Electrodes A, B and C all used a Pb-4%Sb alloy. Electrode A is connected as in ordinary testing. Electrode B is electrically connected to electrode A, but as there are connections through tubules, to the left and right adjacent cells, electrode B's potential should differ from that of electrode A owing to electrolyte resistance. Electrode B simulated that portion of electrode A that is exposed above the electrolyte level, that is, the portion on which corrosion occurs. Electrode C is just immersed in the electrolyte, and not connected electrically. Test conditions were as follows: temperature: 90°C; electrolyte specific gravity: 1.28; current density: 30 mA cm⁻² (in relation to the immersed portion of sample A); duration of test: 10 days.

Table 3 shows the electrode potentials during the test and the state of the electrodes after the test. During the test, the submerged part of electrode A polarized until it attained the hydrogen evolution potential. The submerged part of electrode B had almost the same potential as the exposed portion of electrode A, which approached the Pb/PbSO₄ equilibrium potential. Because electrode C carried no current, it had the open circuit potential of the Pb-4%Sb alloy.

Post-test observations of the samples revealed, for sample A, no corrosion on its submerged portion, while corrosion occurred as before on the portion exposed above the electrolyte level. Sample B corroded on its submerged portion, and the corrosion was similar to that usually observed on exposed electrode portions. Sample B's exposed portion suffered little corrosion. Sample C was hardly corroded at all.

This test showed that if Pb-Sb alloys are maintained near the Pb/PbSO₄ equilibrium potential, it is possible to reproduce negative electrode corrosion. This suggests it was correct to assume a corrosion mechanism whose causes are the local cell reactions which are the hydrogen evolution on Sb and the dissolution of lead.

5. Conclusions

Tests on the corrosion of negative electrodes made of lead alloys showed the following.

Table 3
Electrode potentials during test and electrode appearances after test

	Potential of submerged portions during test (V vs. Pb/PbSO ₄)	Appearance of the electrode after test
Electrode A	-0.58	exposed portion corroded
Electrode B	-0.01	submerged portion corroded
Electrode C	+0.33	hardly any corrosion

(i) Corrosion occurs when test electrodes or counter electrodes contain Sb.

(ii) Corrosion occurs on those portions of electrodes exposed above electrolyte level, inside tiny spaces, and other such locations.

(iii) The higher the electrolyte temperature and the higher its concentration, the faster corrosion proceeds.

(iv) The electrical potential of corroded areas is near the Pb/PbSO₄ equilibrium potential.

We can therefore conclude that negative electrode corrosion consists of local cell reactions which are the hydrogen evolution reaction on Sb and the dissolution of lead. These

occur in areas which have a large electrolyte resistance and which are not sufficiently polarized, such as in thin layers of electrolyte and inside tiny spaces.

References

- [1] P. Ruetschi et al., *J. Electrochem. Soc.*, 111 (1964) 1323.
- [2] A.C. Simon, *J. Electrochem. Soc.*, 114 (1967) 1.
- [3] T. Take et al., *IEICE Tech. Rep. (Jpn.)*, 64 (1986) 331.
- [4] S. Hua et al., *J. Power Sources*, 45 (1993) 131.
- [5] D. Pavlov et al., *J. Electrochem. Soc.*, 142 (1995) 2919.
- [6] R. Wagner, *J. Electrochem. Soc.*, 143 (1996) 139.