

# Study of charge acceptance for the lead-acid battery through in situ EC-AFM observation — influence of the open-circuit standing time on the negative electrode

Yoshiaki Yamaguchi<sup>a,b,\*</sup>, Masashi Shiota<sup>a</sup>, Masaaki Hosokawa<sup>a</sup>, Yasuhide Nakayama<sup>a</sup>,  
Nobumitsu Hirai<sup>b</sup>, Shigeta Hara<sup>b</sup>

<sup>a</sup>Yuasa Corporation, 2-3-21 Kosobe-cho, Takatsuki, Osaka 569-1115, Japan

<sup>b</sup>Department of Materials Science & Processing, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Received 12 September 2000; received in revised form 20 December 2000; accepted 5 April 2001

## Abstract

An influence of the open-circuit standing time after oxidation of the lead electrode was investigated for understanding charge acceptance of the negative electrode of a lead-acid battery. It was confirmed by a potentiostatic transient experiment that charge acceptance of the lead electrode heavily depended on the standing time before charging, and charge acceptance decreased if the standing time was longer. This tendency was conspicuous at the initial period of the reduction process in particular. When the behavior of the lead electrode surface during the open-circuit standing after oxidation was observed by in situ electrochemical atomic force microscope (EC-AFM), it was found that some lead sulfate crystals gradually grow with time to bigger crystals having a smooth surface, retaining basically its morphology of previous one. We have concluded that the standing time dependence of the charge acceptance is caused by this behavior of the crystals. Also, it was confirmed that charge acceptance of a valve regulated lead-acid (VRLA) battery with different standing times can be explained by result of the potentiostatic transient test and the EC-AFM observation. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** In situ observation; EC-AFM; Lead-acid battery; Charge acceptance; Negative electrodes

## 1. Introduction

Charge acceptance of batteries has recently become more important performance as well as specific energy, specific power and life. Since charge acceptance is ability of a battery to accept recharge after discharge, energy efficiency of an application using a battery is affected heavily by this performance. For example, electric vehicles (EV) or hybrid electric vehicles (HEV) have braking-energy recycling system consisted of regenerator and batteries, so that increase of the charge efficiency of batteries leads extension of the mileage [1,2]. In the load leveling (LL) system, improvement of the charge acceptance makes it possible to reduce the electric-cost during the system operation and extend the life of the batteries because the over-charge to the batteries can be suppressed [3,4]. It is therefore, considered that improvement of this performance will become one of the answers to energy saving and the environmental improvement.

We have improved charge acceptance of a lead-acid battery for HEV use, and succeeded in the development of a valve regulated lead-acid (VRLA) battery having charge acceptance twice as high as that of the previous battery [1,2]. However, this charge acceptance is still low compared to that of Ni-MH and Li-ion batteries. In our previous study [1], it was understood that low charge acceptance of the lead-acid battery is caused by the charging characteristics of the negative electrode, therefore reducibility of lead sulfate crystals formed by discharge reaction has to be studied in detail.

To understand reaction process of the negative electrode during discharge/charge cycle, we have applied an electrochemical atomic force microscope (EC-AFM) to in situ observation of the lead sulfate crystals behavior on lead electrode surface during oxidation/reduction cycle. In the first try, we succeeded in direct observation of lead electrode surface in sulfuric acid electrolyte during open-circuit standing and potentiostatic oxidation/reduction cycle. From this result, we also proposed a charge acceptance decline model that electrochemically formed lead sulfate crystals lose their reducibility during open-circuit standing [5]. In the second try, we observed continuously in situ EC-AFM images of

\* Corresponding author. Tel.: +81-726-85-2681; fax: +81-726-85-3070.  
E-mail address: yoshiaki\_yamaguchi@yuasa-jpn.co.jp (Y. Yamaguchi).

lead electrode behavior during a cyclic-voltammetry (CV) measurement, and discussed the reason for the low charge acceptance of the lead-acid battery [6].

Based on these results and proposition, a study was carried out to clarify the mechanism of standing time effect on charge acceptance of the negative electrode. Concretely, we investigated the influence of standing time by using the potentiostatic transient method [7,8] and in situ EC-AFM observation. We also compared these experimental results with charge acceptance of a VRLA battery.

## 2. Experimental

### 2.1. Potentiostatic transient method

In order to investigate the electrochemical behavior of a lead electrode in the oxidation/reduction cycle that corresponds to the discharge/charge cycle of the negative electrode in a lead-acid battery, a potentiostatic transient method was applied for this study. This method consists of applying an oxidative potential step to a lead electrode immersed in sulfuric acid solution, starting from a completely reduced lead surface. Similarly, in the case of lead sulfate reduction after oxidation, a reductive potential step is applied to the electrode. The change of the current density was recorded with time during the whole oxidation/reduction cycle [7]. In this experiment, the reduction current changes were investigated with different open-circuit standing times after oxidation.

The experimental cell used in this method was a conventional three-electrode electrochemical cell. The working electrode was obtained by cutting a pure lead sheet (purity 99.99%). At the beginning, the electrode was mechanically polished by emery paper and fine  $\text{Al}_2\text{O}_3$  powder with pure water to obtain a flat surface. The surface was then chemically etched in a mixed solution of acetic acid and hydrogen peroxide to remove the existing lead oxide layer and the  $\text{Al}_2\text{O}_3$  powders on the surface. After that, the working electrode was washed with pure water and assembled to the cell with an exposed area of approximately  $1.25 \text{ cm}^2$ . Two counter electrodes, which had a total surface area of about  $50 \text{ cm}^2$ , were made of the same pure lead sheet, and assembled to the cell. A  $\text{Hg}/\text{Hg}_2\text{SO}_4$  electrode in  $1.250 \text{ g/cm}^3$  sulfuric acid solution was set in the cell, as a reference electrode. All potentials reported here are referred to this electrode. The cell was filled with  $1.250 \text{ g/cm}^3$  sulfuric acid solution of approximately  $200 \text{ cm}^3$ , which dissolving oxygen in the solution was removed by argon gas bubbling for 3 h before this experiment.

Potentiostatic transient experiments were carried out using a potentiogalvanostat (model HA501G) with a function generator (model HB-105) made by Hokuto Denko Co. The current change was measured with a Digital Scope (model DL716) made by Yokogawa Electric Co. and measuring intervals were 20 ms.

The working electrode was first held at a potential of  $-1400 \text{ mV}$  for 30 min from when the electrolyte was filled

to obtain a complete reduction of its surface. Then the electrode was subjected to 10 cycle of the potentiostatic oxidation/reduction that was constituted with two potential steps of  $-850 \text{ mV}$  for 30 s and  $-1050 \text{ mV}$  for 5 min. It was confirmed that the oxidation and reduction current changes reached an almost constant transient, respectively during the cycling. The rest potential of the working electrode was measured at the end of cycling, which was  $-962 \text{ mV}$ .

After that, the electrode was maintained at the oxidation potential of  $-850 \text{ mV}$  for 30 s, followed by open-circuit standing for 1 min. Then the electrode was reduced again at  $-1050 \text{ mV}$  for 5 min. Similar oxidation/reduction cycles were repeated with different open-circuit standings of 2, 3, 5 and 10 min for the same electrode. All tests were carried out at a temperature of  $25^\circ\text{C}$  in a water bath.

### 2.2. EC-AFM observation

In order to investigate the behavior of lead sulfate crystals formed by oxidation during open-circuit standing, an EC-AFM technique was applied for observation of the lead electrode surface in sulfuric acid solution.

In this study, we used an EC-AFM unit made by Molecular Imaging (MI) Co. with a control unit made by Digital Instruments (DI) Co. (model NanoScope IIIa) for in situ observation. The AFM experiments were performed utilizing a commercial  $\text{Si}_3\text{N}_4$  cantilever with integral Au coated tips, a  $\text{PbO}_2$  electrode as a counter electrode, and a  $\text{Hg}/\text{Hg}_2\text{SO}_4$  electrode in  $1.250 \text{ g/cm}^3$   $\text{H}_2\text{SO}_4$  solution as a reference electrode for the electrochemical cell. The electrochemical operations in this experiment were carried out by using a potentiogalvanostat (model HA501G) with a function generator (model HB-105) made by Hokuto Denko Co.

The cell was set up and a pure lead electrode was treated by the similar process of the above potentiostatic transient method. It was confirmed by the EC-AFM during 10 cycles of oxidation/reduction that many small lead crystals were formed on the lead electrode at the oxidation of  $-850 \text{ mV}$  and the crystals were completely reduced by the maintenance of  $-1050 \text{ mV}$  for 5 min. The rest potential of the working electrode was measured at the end of cycling, which was found  $-960 \text{ mV}$ .

After that, the electrode was maintained again at the oxidation potential of  $-850 \text{ mV}$  for 30 s, then it was kept at open-circuit for 10 min. The surface morphology of the electrode during the open-circuit standing was observed directly by the EC-AFM. The AFM observation area was  $5 \mu\text{m} \times 5 \mu\text{m}$ . All the tests were maintained at a temperature of  $25^\circ\text{C}$  and carried out in an argon gas chamber to avoid oxidation of the electrode, which is caused by oxygen from air.

### 2.3. Charge acceptance of VRLA battery

To compare the behavior in the result of the above electrochemical experiment with that of a lead-acid battery,

charge acceptance of a VRLA battery was measured under the following conditions.

The test battery was a 21 Ah (5 HR) VRLA cell, and its charge acceptance (W/kg) at a 2.5 V constant voltage was examined at each depth of discharge (DOD) and open-circuit standing time after discharge. The battery was discharged with a current of 7 A until 0, 30, 50 and 80% DOD of the 5 HR capacity from the fully charged state. Open-circuit standing times were 0 s, 10 s and 10 min. All the tests were maintained at a temperature of 25°C. Each charge acceptance was calculated with both of the voltage and the current obtained after 10 s in charging.

### 3. Results and discussion

Fig. 1 shows the potentiostatic transient of the 1 min open-circuit standing experiment. Similar data were also obtained in other open-circuit standings, 0, 2, 3, 5 and 10 min, respectively. The period A is oxidation at  $-850$  mV for 30 s, the period B is open-circuit standing for 1 min and the period C is reduction at  $-1050$  mV for 5 min in this figure. The detailed transients at the oxidation part of all the potentiostatic experiments are shown in Fig. 2. As can be seen here, these transients were almost the same through the whole experiments, and the

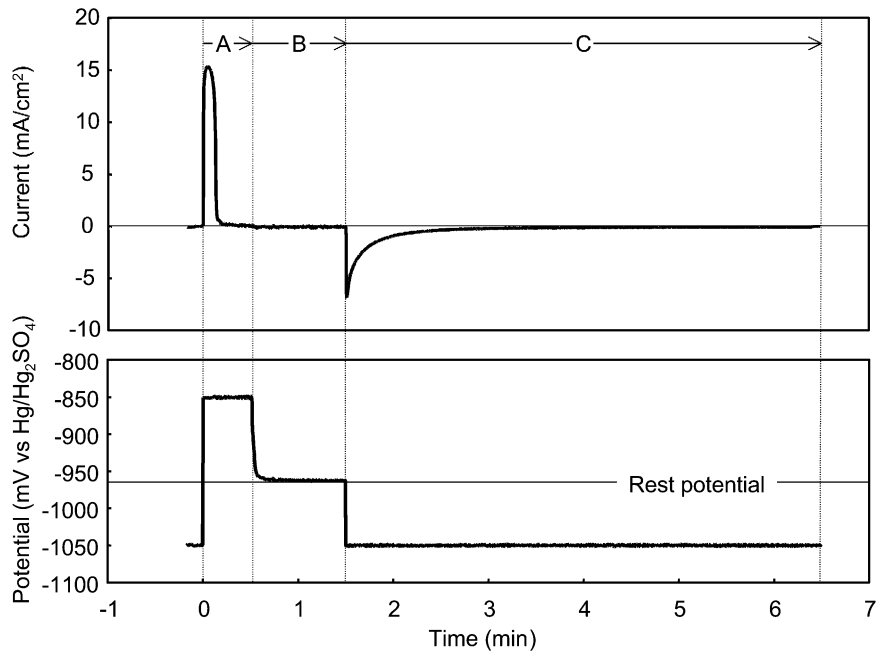


Fig. 1. A potentiostatic transient of the 1 min open-circuit standing experiment: period A, oxidation at  $-850$  mV vs.  $\text{Hg}/\text{Hg}_2\text{SO}_4$  for 30 s; period B, open-circuit standing for 1 min; period C, reduction at  $-1050$  mV vs.  $\text{Hg}/\text{Hg}_2\text{SO}_4$  for 5 min.

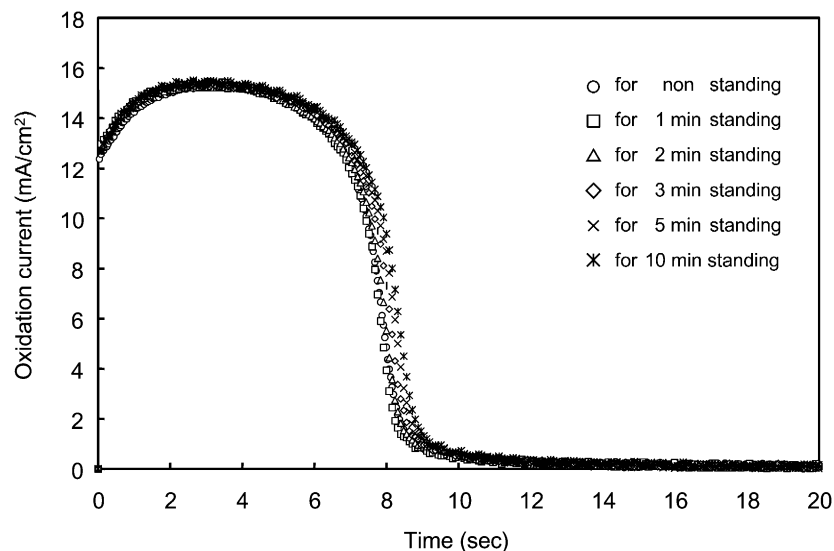


Fig. 2. Oxidation transients of each open-circuit standing time experiment.

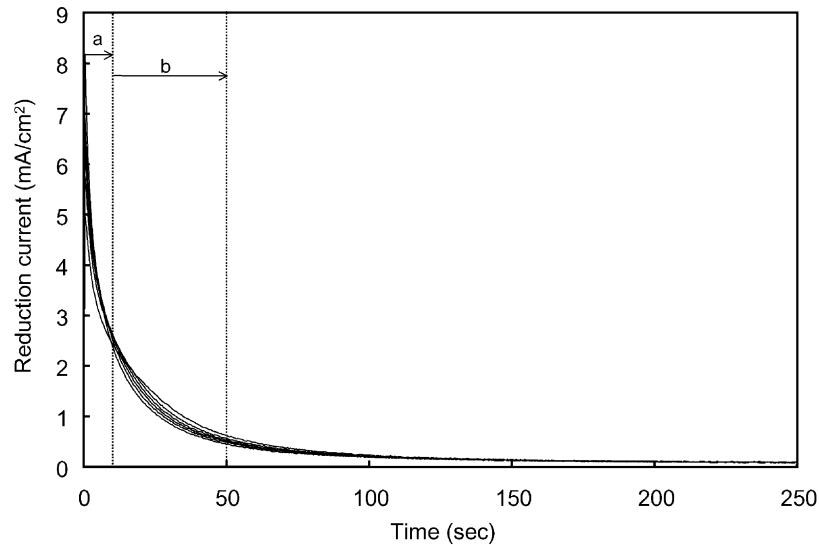


Fig. 3. Reduction transients after each open-circuit standing time. Period 'a' is magnified in Fig. 4. Period 'b' is magnified in Fig. 5.

capacity of the working electrode was approximately  $42 \mu\text{Ah}$ .

The transients at the reduction part are shown in Figs. 3–5 thereby, it shows the detailed reduction transients for 0–10 and 10–50 s in Fig. 3, respectively. It was found in Fig. 4 that charge acceptance of the lead electrode heavily depended on the standing time, and it decreased when the standing time was longer. However, tendency of the transients reversed completely after 10 s of the reduction as shown in Fig. 5. These results on reduction transient can well be explained by a charge acceptance decline model [5], where a passive lead sulfate crystal is considered to be formed from the lead sulfate on the electrode surface to cover an active lead sulfate crystal formed by electrochemically reaction, during open-circuit standing (Fig. 6). We consider that since the

passive crystal layer on the active crystal becomes thicker with a longer standing time, charge acceptance at the initial period of reduction decreases as shown in Fig. 4. After the passive crystal covering the active crystal would be totally reduced, the active crystal starts to be reduced at a higher current in the medium term of the reduction as shown in Fig. 5.

Fig. 7 shows the relation of the reduction/oxidation ratio, the reduction period and open-circuit standing time, obtained in this experiment. The reduction/oxidation ratio corresponds to the state of charge of the electrode, so that charge acceptance is higher if the ratio is larger. From this figure, it was found that charge acceptance is higher if the open-circuit standing time is shorter, up to 15 s reduction. In EV or HEV, the charging period by their regenerating system

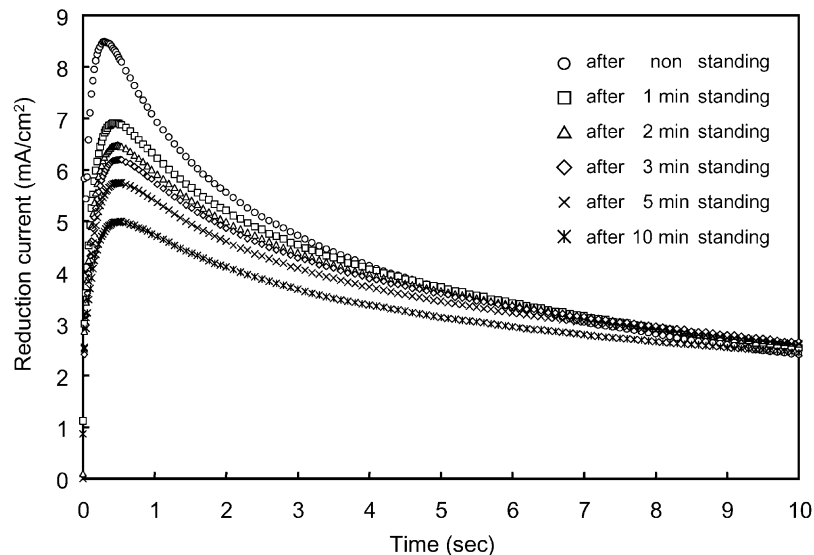


Fig. 4. Reduction transients for 0–10 s after each open-circuit standing time.

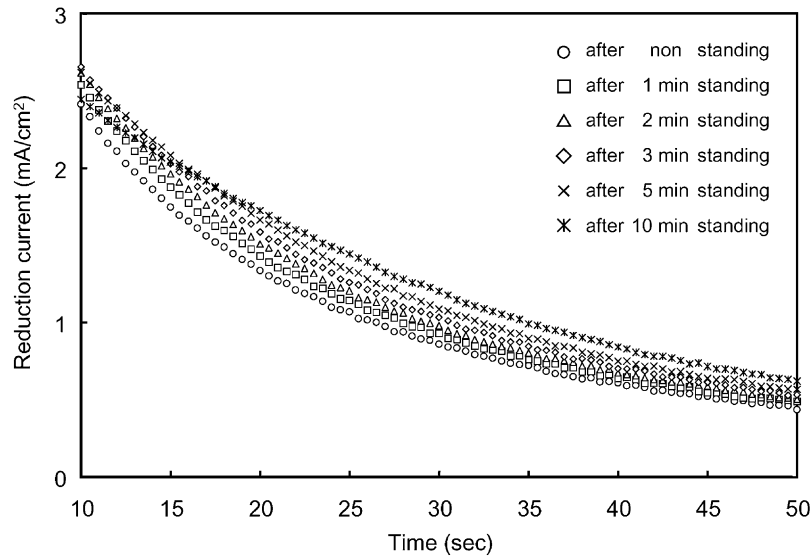


Fig. 5. Reduction transients for 10–50 s after each open-circuit standing time.

is <10 s, so charge acceptance of their batteries would be influenced strongly by the standing time.

We observed morphology change of the lead electrode surface during open-circuit standing by EC-AFM observation to investigate the behavior of lead sulfate crystals in detail. Fig. 8 shows semi-continuously AFM images observed. And Fig. 9 shows four magnified images of Fig. 8 and the images correspond to a same part of the 0, 3, 5 and 10 min image, respectively. Morphology of the electrode surface changed extremely during the standing.

Although, there were a lot of small lead sulfate crystals <1 μm in size on the electrode surface immediately after oxidation, some of them gradually grew with time to bigger crystals with a smooth surface. During that time, other many crystals that were less than 0.5 μm in size were dissolved. This demonstrates that dissolution and re-crystallization of lead sulfate crystals occur during the open-circuit standing and the reaction is quite fast. In general, reduction of bigger crystal is difficult and the total surface energy of a smooth crystal is low. Therefore, the open-circuit standing time

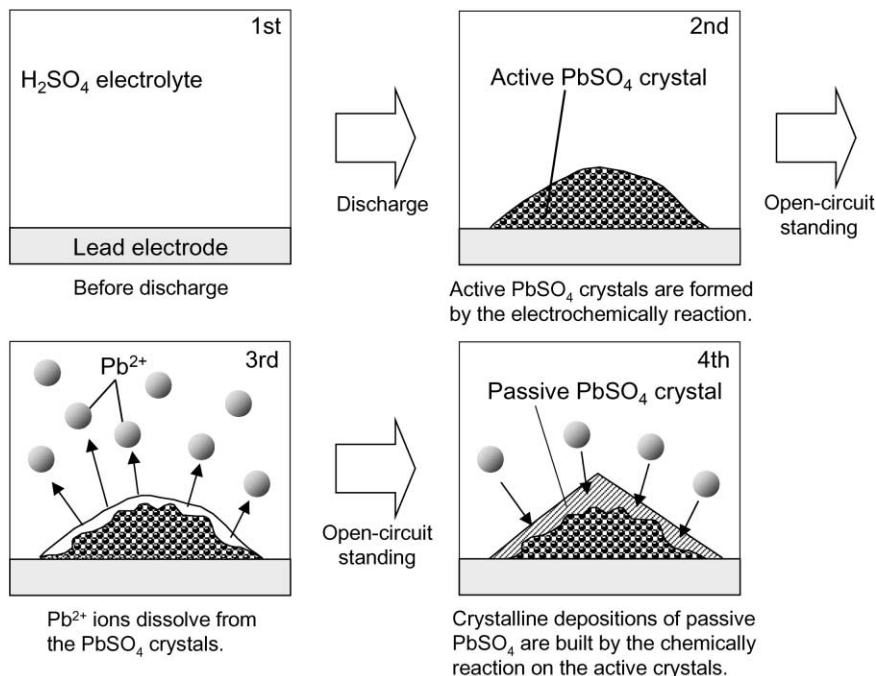


Fig. 6. A charge acceptance decline model by open-circuit standing after discharge on the negative electrode of lead-acid battery [5].

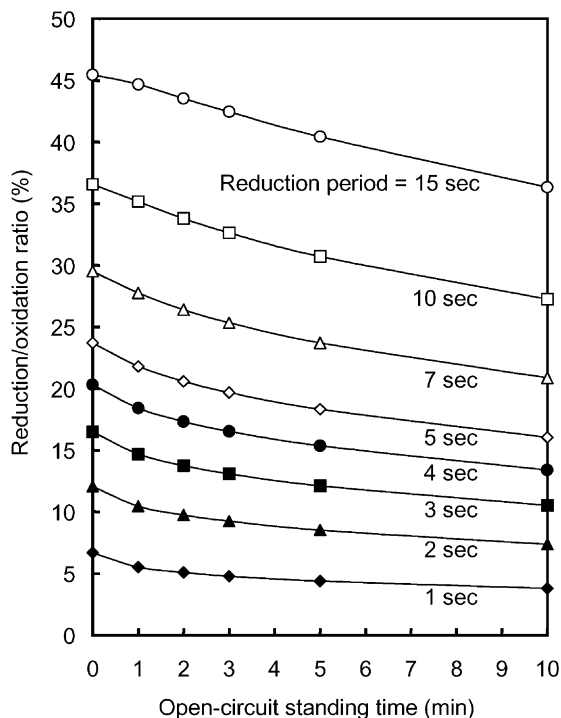


Fig. 7. Relation of the reduction/oxidation ratio, the reduction period and the open-circuit standing time.

dependence on charge acceptance would probably be caused by these behaviors of lead sulfate crystals.

It was also found that crystals at the 10 min picture retain the basic image of the previous ones. This suggests the existence of active lead sulfate at the core of a crystal, which is agreement with the understanding of the result of the potentiostatic transient experiment.

To compare with these results of the fundamental experiments, charge acceptance of a VRLA battery was investigated with different open-circuit standing times after discharge. Fig. 10 shows its result. It was found that charge acceptance decreased also with longer open-circuit standing time at every DOD state of the battery. This tendency obviously corresponds to the result of the potentiostatic transient experiment of the lead electrode. It was considered in our previous study that characteristics of charge acceptance are mainly caused by negative electrode behavior, although both behaviors of the positive and the negative electrode might affect as well [1]. Therefore, this result with a battery can be explained by the same mechanism as described in the AFM examination.

In this way, charge acceptance of the present lead-acid battery is strongly influenced by the open-circuit standing time after discharge. Therefore, the following technologies on the lead-acid battery should be developed for its effective

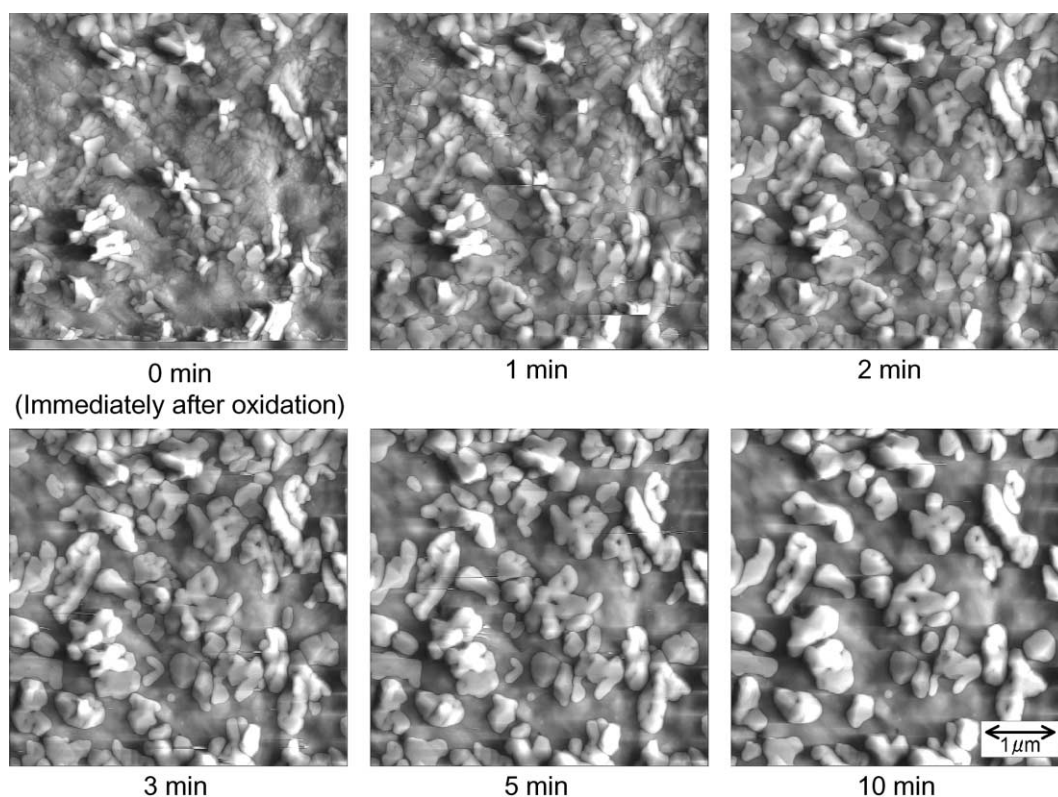


Fig. 8. Behavior of lead sulfate crystals during open-circuit standing after oxidation, observed by AFM.

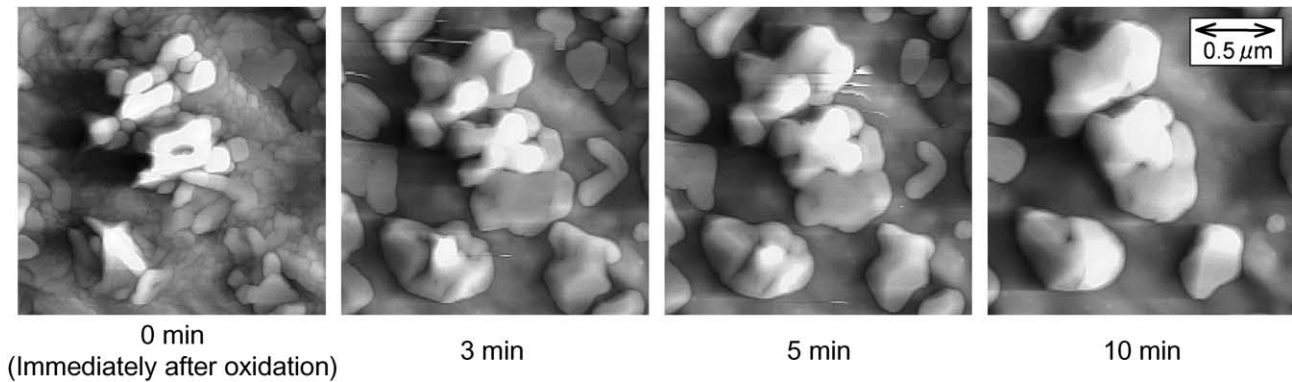


Fig. 9. Magnified AFM images of Fig. 8.

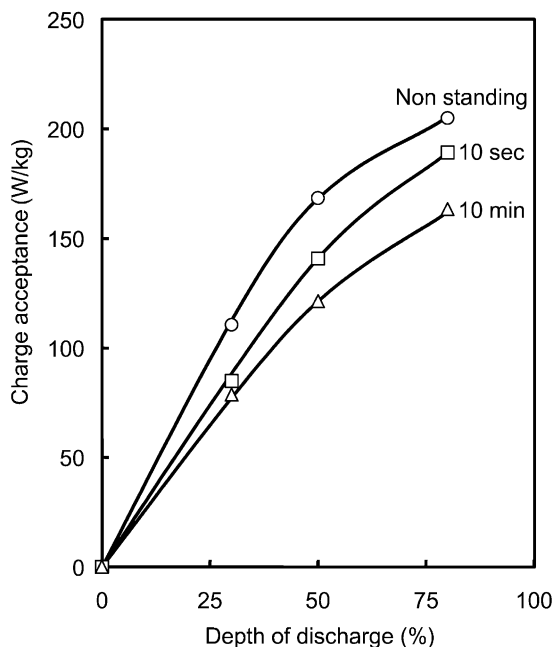


Fig. 10. Charge acceptance of a VRLA battery with different open-circuit standing times after discharge.

use, improvement of lead sulfate crystal's activity, together with a method to maintain its activity during open-circuit standing.

#### 4. Conclusions

The influence of open-circuit standing for charge acceptance of the lead-acid battery was investigated by the potentiostatic transient method, in situ EC-AFM observation and testing of a VRLA battery. The experimental results led to the following conclusions.

1. Charge acceptance of the lead electrode quite depends on the open-circuit standing time at the initial period of

the reduction process, and it decreases if the standing time is longer, as suggested by the potentiostatic transient experiment.

2. It was found by the in situ EC-AFM observation that during the open-circuit standing some lead sulfate crystals gradually grow to bigger crystals having a smooth surface, with many other crystals dissolving.
3. It was also found by the EC-AFM observation that the grown crystal image during standing retains that of the previous one.
4. It was confirmed that the tendency of charge acceptance of a VRLA battery with different standing times meets the result of the potentiostatic transient test.
5. All the results in this study can be well explained by the charge acceptance decline model, where a passive lead sulfate crystal is considered to be deposited to cover an active crystal formed by the electrochemical reaction during open-circuit standing.

#### References

- [1] K. Hasegawa, M. Hosokawa, N. Matsumoto, N. Yamada, S. Takahashi, Y. Nakayama, in: Proceedings of the 13th International Electric Vehicle Symposium (EVS-13), Vol. 1, 1996, pp. 489–494.
- [2] M. Hosokawa, N. Yamada, K. Hasegawa, Y. Nakayama, M. Yokoh, K. Ariga, T. Takeda, in: Proceedings of the 16th International Electric Vehicle Symposium (EVS-16) CD-ROM, 1999.
- [3] K. Hirakawa, S. Takahashi, M. Morimitsu, Y. Yamaguchi, Y. Nakayama, YUASA-JIHO 87 (1999) 42–46 (in Japanese).
- [4] S. Takahashi, K. Hirakawa, M. Morimitsu, Y. Yamaguchi, Y. Nakayama, YUASA-JIHO 88 (2000) 34–38 (in Japanese).
- [5] Y. Yamaguchi, M. Shiota, Y. Nakayama, N. Hirai, S. Hara, J. Power Sources 85 (2000) 22–28.
- [6] Y. Yamaguchi, M. Shiota, Y. Nakayama, N. Hirai, S. Hara, J. Power Sources 93 (2001) 104–111.
- [7] C. Francia, M. Maja, P. Spinelli, F. Saez, B. Martinez, D. Marin, J. Power Sources 85 (2000) 102–109.
- [8] C. Francia, M. Maja, P. Spinelli, J. Power Sources 85 (2000) 110–116.