

In situ analysis of electrochemical reactions at a lead surface in sulfuric acid solution

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Abstract

An Atomic Force Microscope (AFM) was used to analyze the surface of a lead plate when the reaction corresponding to what occurs at the negative electrode of a lead acid battery, $\text{Pb} + \text{SO}_4^{2-} \rightleftharpoons \text{PbSO}_4 + 2\text{e}$, took place. At the beginning, when the lead plate, on the surface of which lead oxide already existed, was in contact with sulfuric acid, lead sulfate crystals were formed and gradually grew with time without applying any potential. In situ AFM observation of the formation and the growth of lead sulfate at the potential corresponding to the discharge reaction was attempted. And it was possible along with the reduction of the lead sulfate, which formed in discharging process. The results also showed that the chemically formed lead sulfate crystals were clearly different in appearance from the electrochemically formed ones. These results were also applied to a study of the mechanism of the sulfation process that often occurs in the active material of the negative electrode of a lead acid battery. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lead acid battery; In situ analysis; AFM; Negative electrodes; Sulfation

1. Introduction

Since Planté developed the lead acid battery in 1860 [1], it has been used as a main rechargeable battery all over the world, for example, for the SLI and UPS use. We are now developing a novel lead acid battery aimed at electric vehicles, load-leveling and other new applications.

Since such a battery is required to have a high performance on specific energy (Wh/kg), specific power (W/kg) and long life cycles, it is important to analyze the detailed role of the active material reactions for the design. Because such a detailed understanding of the surface reaction was impossible with conventional techniques so far, we applied here a new method for in situ observation of the reaction process by an Atomic Force Microscope (AFM). There are no trials by the AFM to analyze the electrochemical reactions in a lead acid battery until now.

The AFM is a kind of Scanning Probe Microscope (SPM), and it does not require high vacuum condition for the observation, unlike Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). Moreover, AFM has a high resolution like that of TEM. It is essential to observe the material surface under the given environment. Indeed, it has become popular to use AFM for the study of the electrochemical reaction and atomic level images in solution have been observed [2–4].

In this study, we succeeded in the direct observation of the lead electrode surface in sulfuric acid solution during the reaction, $\text{Pb} + \text{SO}_4^{2-} \rightleftharpoons \text{PbSO}_4 + 2\text{e}$, in the lead acid battery.

2. Experimental

2.1. AFM equipment and electrochemical cell

The surface of the lead sheet samples used in these experiments were polished and washed in ethanol. In this

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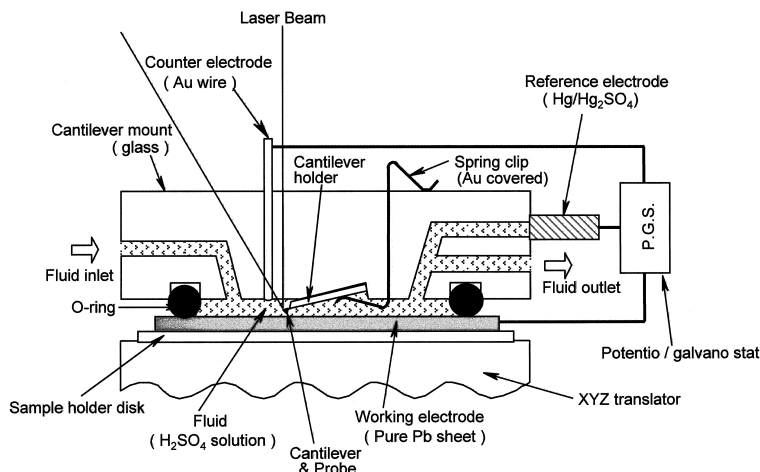


Fig. 1. Cross-sectional image of the EC-AFM cell. Laser beam.

study, we used an electrochemical AFM (EC-AFM) unit by DI (model NanoScope II) for in situ observation for the electrochemical reaction, $\text{Pb} + \text{SO}_4^{2-} \rightleftharpoons \text{PbSO}_4 + 2\text{e}^-$. Fig. 1 shows a cross-sectional image of the EC-AFM cell used in this study. EC-AFM experiments were performed utilizing a commercial Si_3N_4 cantilever with integral Au coated tips.

2.2. AFM image observation

The first observation was of the chemical reaction of a pure lead electrode under water or a sulfuric acid solution. The lead sheet sample was assembled in the cell, and hence the surface was observed under air. The successive

observation was made after filling the cell with water. A similar observation was then made after substituting water with sulfuric acid. The sulfuric acid concentration was 0.05 M in this experiment. The observation area was $10 \times 10 \mu\text{m}$, and observation was made in the Force Mode of the NanoScope II. The experiment was performed at room temperature.

Next, observed was the electrochemical reaction of a pure lead electrode with sulfuric acid solution under a reduction or oxidation potential which was corresponding to charge or discharge reaction of the negative electrode in the lead acid battery. In this observation, a similar cell was assembled and filled with 1.25 sp. gr. sulfuric acid electrolyte. A potential was applied by the potentiostat and

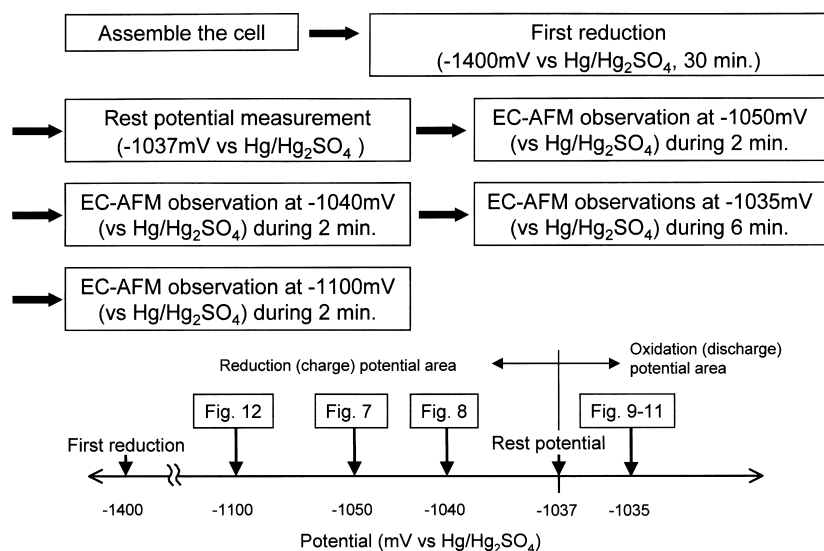


Fig. 2. Potential operation and observation way of EC-AFM. Assemble the cell.

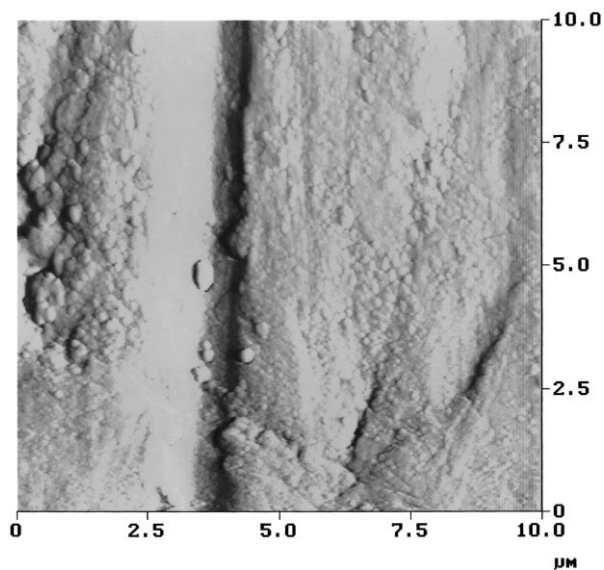


Fig. 3. AFM image of lead surface in air at room temperature.

measured vs. an $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode. The in situ surface morphology change was observed by AFM when the potential was changed as follows. Step 1: complete reduction at -1400 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ for 30 min. Step 2: the rest potential of the sample was measured, which was found -1037 mV. Step 3: maintained at -1050 mV for 2 min within a AFM observation. Step 4: maintained at -1040 mV for 2 min within a AFM observation. Step 5: oxidation at -1035 mV for 6 min during which three AFM image observations were made. Step 5: reduction at -1100 mV for 2 min within an AFM image capture. This mode of operation is shown in Fig. 2. The

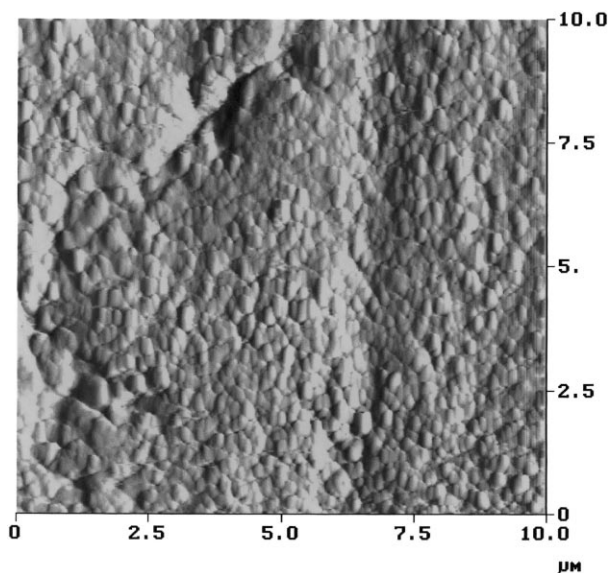


Fig. 4. AFM image of lead surface in pure water after holding for 20 min at room temperature.

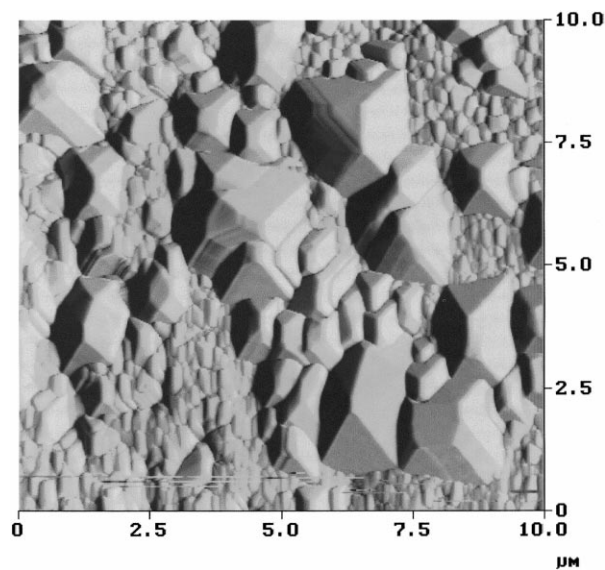


Fig. 5. AFM image of lead surface in 0.05 M sulfuric acid after holding for 20 min at room temperature.

observation area was 5×5 μm , by using the Force Mode of the NanoScope II at room temperature.

3. Results and discussion

3.1. Surface morphology change by chemical reaction

AFM images of the lead surface in various conditions are shown as Figs. 3–6. Figs. 3–6 are AFM images of the

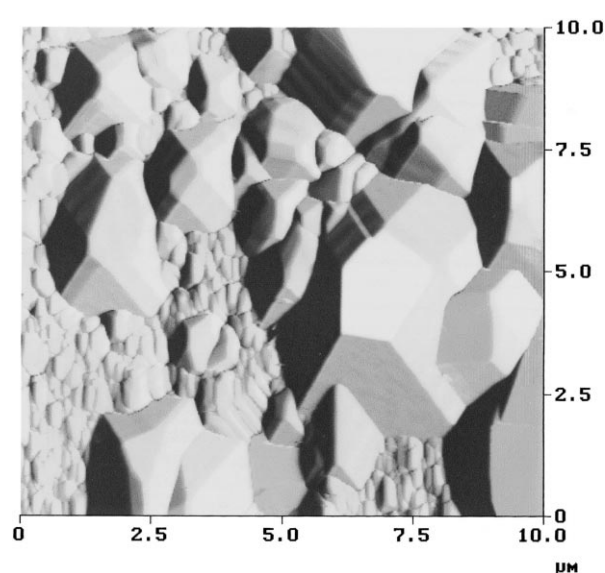


Fig. 6. AFM image of lead surface in 0.05 M sulfuric acid after holding for 60 min at room temperature.

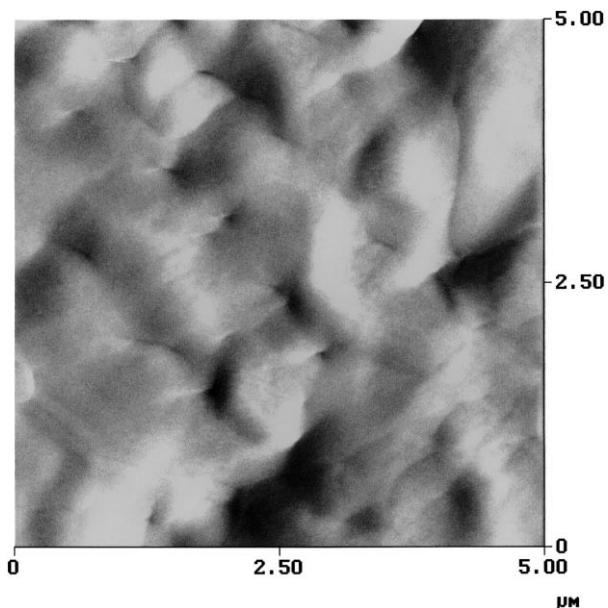


Fig. 7. AFM image of lead surface in 1.25 sp. gr. sulfuric acid under reduction potential after holding for 2 min at room temperature; under -1050 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$.

lead surface in air, in water after holding for 20 min, in 0.05 M sulfuric acid after holding for 20 min, and in 0.05 M sulfuric acid after holding for 60 min, respectively.

With these images, it was found that the lead surface was covered with a lead oxide film caused by water and the lead sulfate crystals grew up on the surface in sulfuric acid. Moreover, the lead sulfate crystals formed by this reaction had very flat surfaces as observed also by SEM.

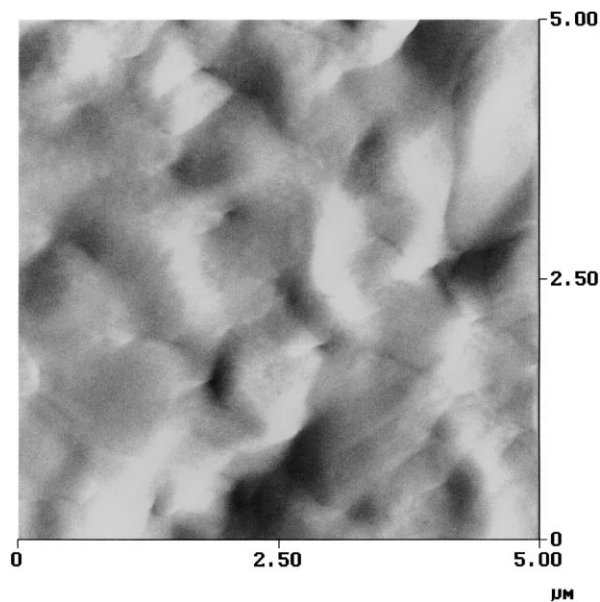


Fig. 8. AFM image of lead surface in 1.25 sp. gr. sulfuric acid under reduction potential after holding for 2 min at room temperature; under -1040 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$.

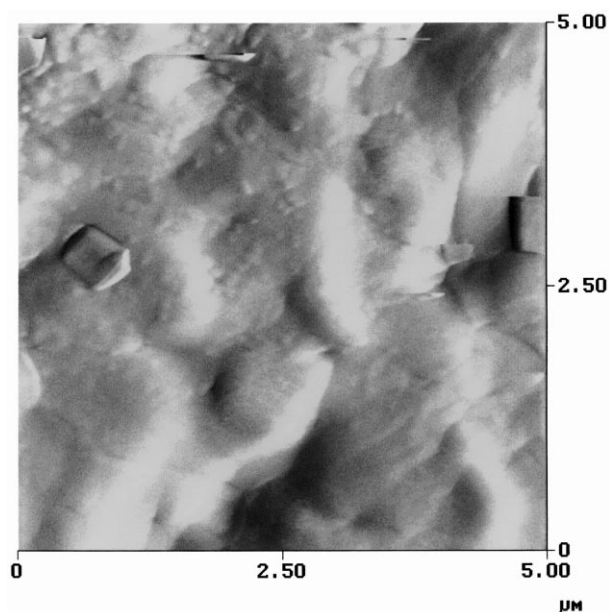


Fig. 9. AFM image of lead surface in 1.25 sp. gr. sulfuric acid under oxidation potential after holding for 2 min at room temperature; under -1035 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$.

From these experiments, it was proved that AFM could be used to observe morphology changes on lead surface in the sulfuric acid solution.

3.2. Surface morphology change by electrochemical reaction

A series of AFM images on the lead electrode surface under reduction and oxidation potentials are shown as

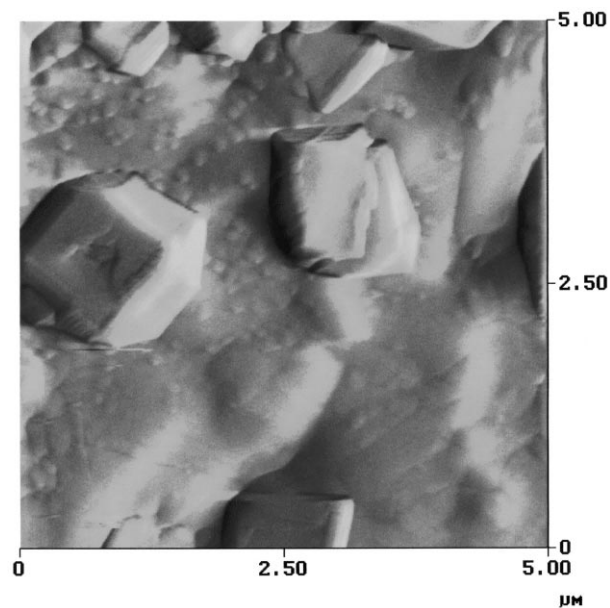


Fig. 10. AFM image of lead surface in 1.25 sp. gr. sulfuric acid under oxidation potential after holding for 4 min at room temperature; under -1035 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$.

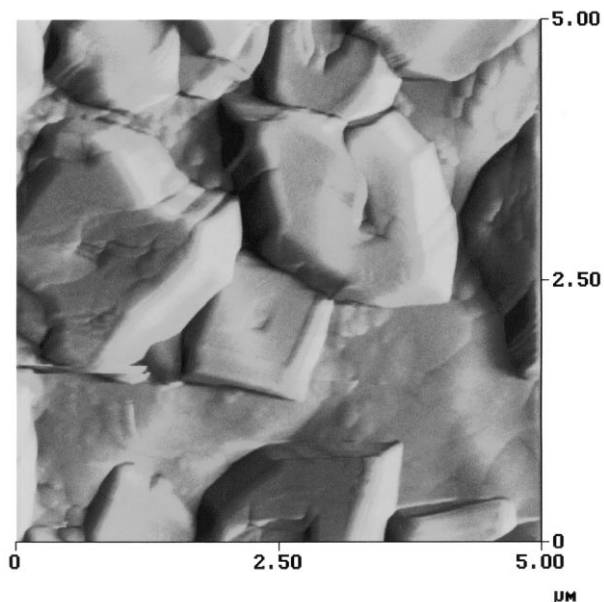


Fig. 11. AFM image of lead surface in 1.25 sp. gr. sulfuric acid under oxidation potential after holding for 6 min at room temperature; under -1035 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$.

from Figs. 7–12. Figs. 7 and 8 are equivalent to the charging condition in a lead acid battery. Only the clean metallic lead surface is seen in these images.

Figs. 9–11 are obtained under the discharging condition at -1035 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$. Since the rest potential of the sample was -1037 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$, the potential here was set at $+2$ mV higher than the rest potential. Lead sulfate crystals appeared at the moment when the potential was set at -1035 mV and then grew with time. By these images, it was found that the lead sulfate crystals formed by the electrochemical reaction were different from those formed by the chemical reaction, the former surface was rougher.

Finally, Fig. 12 is taken under the recharging condition. The morphology of the lead sulfate crystals, formed by the oxidation reaction, changed at the moment when the potential was set at -1100 mV, and the crystals continuously dissolved with time until they disappeared.

3.3. Proposed sulfation model

It was found that there are differences in chemically and electrochemically formed lead sulfate crystals in this experiment, as shown in Fig. 13. The chemically formed crystal has a very flat surface and the electrochemically formed one has a rough surface. In this case, it is considered generally that the crystal with a flat surface may have a high density or is a single-crystal. On the other hand, the crystal with a rough surface may contain many vacancies or is made of poly-crystals. Therefore, it is considered that the chemically formed crystal has a low activity but the

electrochemically formed crystal has a high activity, the difference in their activities being the key for sulfation.

Sulfation, which is one of the failure modes of the negative active material in the lead acid battery, is considered to be due to lead sulfate crystal having low activity. This change in activity has been generally explained by continuous growing of lead sulfate crystals. But, even if the large crystal was not found in the negative active material, sulfation sometimes occurred. Therefore, we propose here a new model of the sulfation mechanism as shown in Fig. 14.

The first illustration in Fig. 14 shows a lead electrode in sulfuric acid electrolyte before the discharging process. Lead sulfate crystals are formed on it by a discharge process shown at the second illustration. Since the crystals formed electrochemically (see right image in Fig. 13), have a higher activity, lead ions will dissolve easily into the electrolyte from lead sulfate crystals during subsequent standing at an open circuit, as shown at the third illustration in Fig. 14. And moreover during an even longer standing, lead ions re-crystallize as a new lead sulfate crystal on the old crystals by a chemical reaction, by Ostwald's ripening. The image of this phenomenon is shown in the final drawing at Fig. 14. Consequently, whole of the crystal loses charge acceptability, because the new lead sulfate crystal has a low activity.

4. Conclusions

Using EC-AFM equipment for the in situ observation of the lead electrode surface, the reaction that occurs on the

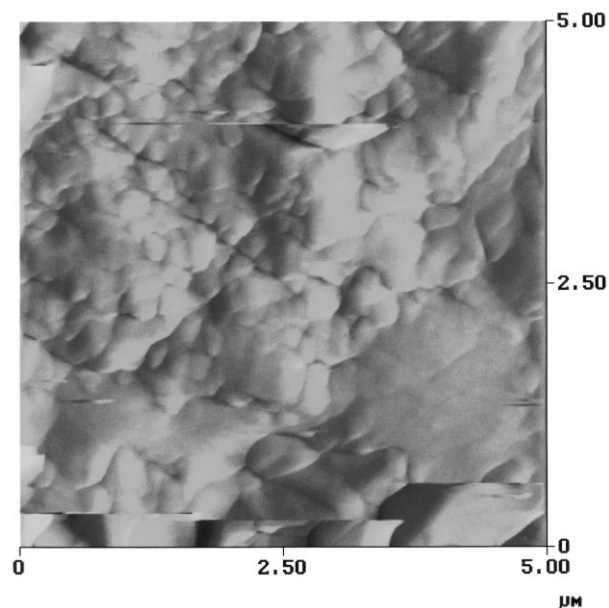


Fig. 12. AFM image of lead surface in 1.25 sp. gr. sulfuric acid under reduction potential after holding for 2 min at room temperature; under -1100 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$.

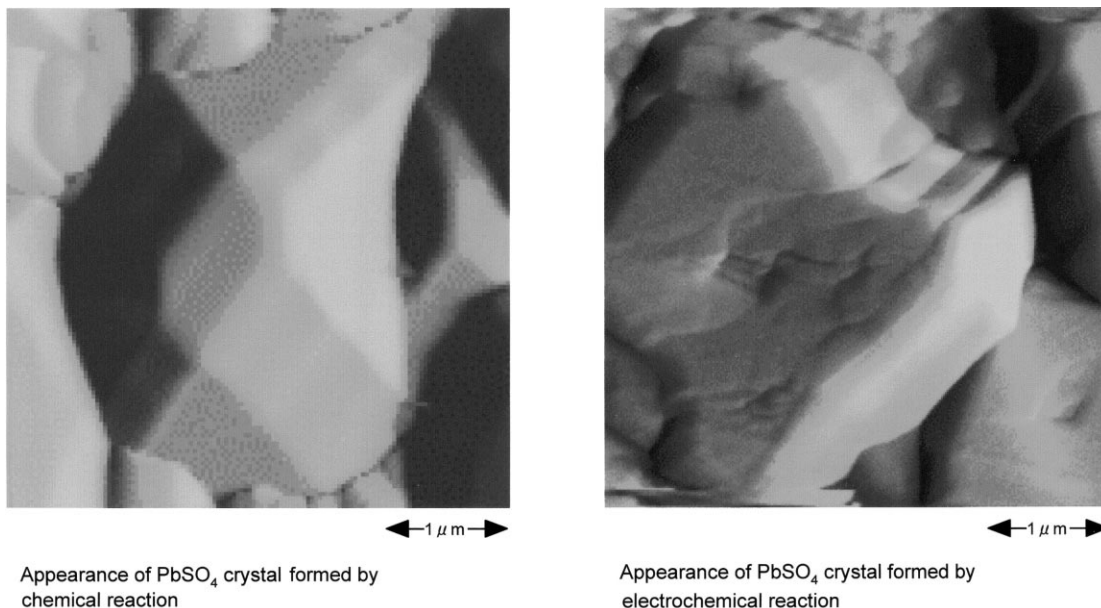


Fig. 13. Difference between chemically and electrochemically formed PbSO₄ crystals. Appearance of PbSO₄ crystal.

electrode surface could be observed directly. The experiments performed under various conditions (air, water, and sulfuric acid solution) led to the following conclusions.

1. When a lead plate, on the surface of which lead oxide existed, was in contact with sulfuric acid, lead sulfate crystals formed, and gradually grew with time.

2. In situ observation was possible with regard to the formation and the growth of lead sulfate crystals at the potential corresponding to the discharge reaction.

3. In situ observation was also possible with regard to the reduction process of the lead sulfate crystals that were previously formed during discharging.

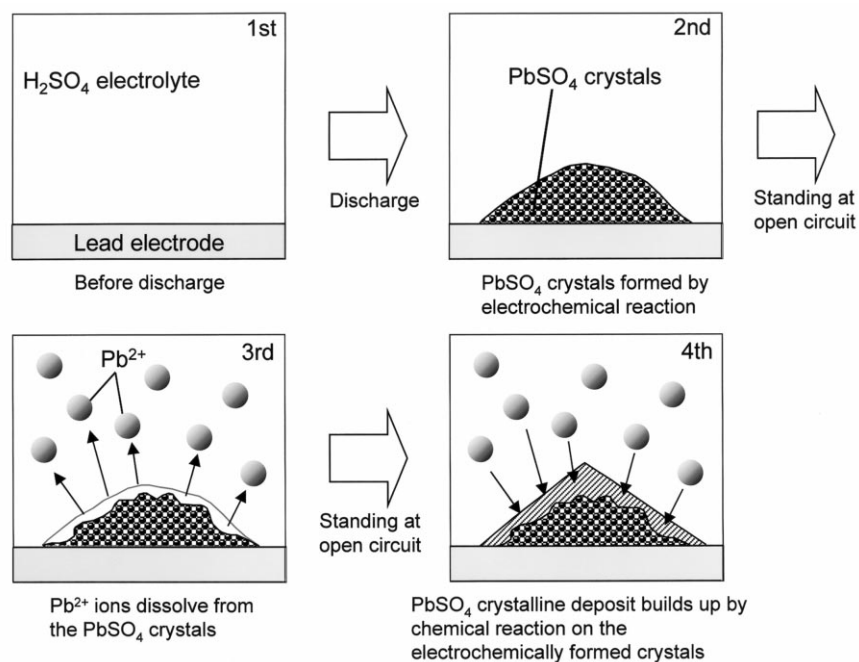


Fig. 14. New model of sulfation at negative active material for lead acid battery. H₂SO₄ electrolyte; Lead electrode; Before discharge; Discharge; PbSO₄ crystals; PbSO₄ crystals formed by electrochemical reaction; Standing at open circuit; Pb²⁺; Pb²⁺ ions dissolve from the PbSO₄ crystals; Standing at open circuit; PbSO₄ crystalline deposit builds up by chemical reaction on the electrochemically formed crystals.

4. AFM observations revealed that chemically formed lead sulfate was clearly different in appearance from electrochemically formed lead sulfate.

5. A new sulfation mechanism was proposed that takes into consideration the change in surface activity of the different formed lead sulfate crystals (i.e., chemical or electrochemical).

6. In situ observations by AFM are useful tools for further development of lead acid battery with a high performance.

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