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Application News

No. S41

Surface Observation

Visualization of the Additive Layer in Vicinity of Negative Electrode in Electrolyte Using SPM-8100FM and Electrochemical Solution Cell in Secondary Batteries

Introduction

The charging and discharging characteristics, durability, and other performance of secondary batteries, represented by lead acid batteries and lithium ion batteries, have been enhanced by addition of additives to the electrolyte. To date, however, how those additives contribute to improvement of battery performance still has not been clarified. Observation of the interface state in the vicinity of the negative electrode in the electrolyte is important for elucidating the contribution of the additive. This paper reports the first successful visualization of the lignin-lead (Pb) layer by cross-sectional imaging of the vicinity of the negative electrode (Pb) in a lead acid battery by using an SPM-8100FM high-resolution scanning probe microscope and an electrochemical solution cell. Use of the frequency modulation (FM) method in the SPM-8100FM enables detection of smaller force than is possible by conventional atomic force microscopy (AFM).

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Lead Acid Batteries

Lead acid batteries are a type of secondary battery that possesses various advantages, including excellent safety, a wide operating temperature range, and discharge of a large current. For these reasons, they are widely used in uninterruptible power supply (UPS) devices, emergency power supply equipment for public facilities, and starting batteries for automotive engine start-stop systems, and thus have become an indispensable part of the social infrastructure. However, sulfation is known to be a problem in this type of battery, as it causes deterioration of battery performance [1], [2]. Fig. 1 shows a schematic diagram of the sulfation phenomenon, in which lead sulfate generated by the discharge reaction is crystallized and hardened on the negative electrode. Additives are added to the dilute sulfuric acid used as the electrolyte in order to alleviate this problem. Sulfonated lignin [3] (hereinafter, lignin) is a representative additive. However, even though observation by contact mode AFM has been reported, how lignin contributes to the electrochemical reaction and alleviation of sulfation still has not been clarified until now.

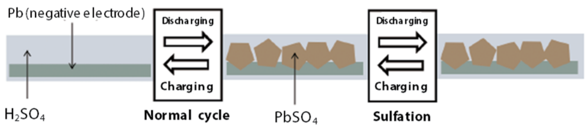


Fig. 1 Schematic Diagram of Negative Electrode and Sulfation

SPM-8100FM

Fig. 2 shows the SPM-8100FM. High-resolution observation and measurement is realized in this instrument by adoption of the frequency modulation method (FM method), which reduces noise in the atmosphere and in solutions to 1/20 of the conventional level.

Fig. 2 SPM-8100FM High-Resolution Scanning Probe Microscope

Results and Discussion

Fig. 3 and Fig. 4 show images of the vicinity of the negative electrode (Pb) by cross-sectional imaging after the initial reduction reaction (initial state as cell). In these, the sample is viewed from the cross-sectional direction. The upper part of the images is the dilute sulfuric acid side, that is, the electrolyte, and the position where the bright area in the lower part of the image changes to dark is the Pb surface. Parts where the probe detects force (repulsion) appear bright.

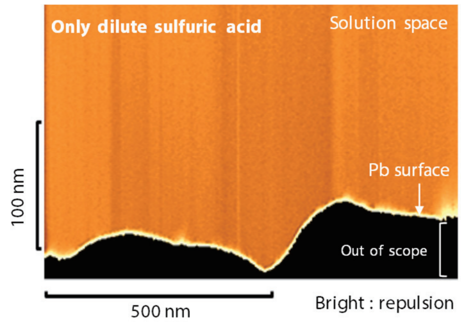


Fig. 3 Only Dilute Sulfuric Acid: Image of Vicinity of Negative Electrode (Pb) by Cross-Sectional Imaging

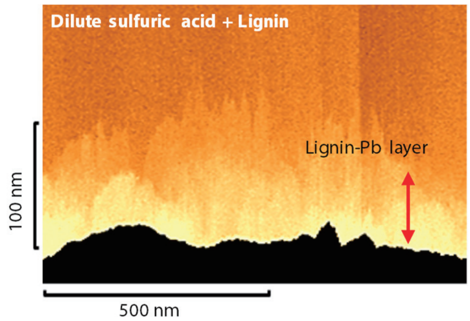


Fig. 4 Dilute Sulfuric Acid + Lignin: Image of Vicinity of Negative Electrode (Pb) by Cross-Sectional Imaging

In the case of "Only dilute sulfuric acid" in Fig. 3, a distinctive contrast cannot be observed above the Pb surface. On the other hand, in the case of "Dilute sulfuric acid + lignin" in Fig. 4, a distinctive contrast can be seen above the Pb surface, as indicated by the red arrow in the figure. Because this distinctive contrast does not exist when only dilute sulfuric acid is used as the electrolyte, it is thought that this layer is a lignin-Pb, and this layer contributes to reduction of sulfation. The bright contrast of the lignin-Pb layer indicates that the probe has penetrated into the layer, and at the same time, also shows that the lignin-Pb layer is adsorbed on the Pb surface in a soft state. (Because lead is harder than the probe, the probe cannot penetrate into the Pb itself.)

Conclusion

Cross-sectional imaging of the vicinity of Pb in dilute sulfuric acid was conducted using a SPM-8100FM and an electrochemical solution cell. As a result, it was possible to visualize a lignin-Pb layer having a thickness from 50 nm to 100 nm on the surface of the Pb after the initial reduction reaction for the first time. Application of analysis by cross-sectional imaging in electrolytes to analyses of other types of secondary batteries and the corrosion protection processes of metals can also be expected.

Principle

Fig. 5 shows a schematic diagram of the frequency modulation method (FM method). Unlike the conventional amplitude modulation method (AM method), the FM method detects the force of interaction acting between the probe and the sample as a change of the resonance frequency of the cantilever Δf. By reducing the displacement conversion noise density to 20 fm/√Hz or less, cantilever oscillation can also be reduced in the SPM-8100FM method in comparison with the conventional technique. This enables detection of force in the atmosphere and in solutions with more than 20 times greater sensitivity than with the conventional AM method.

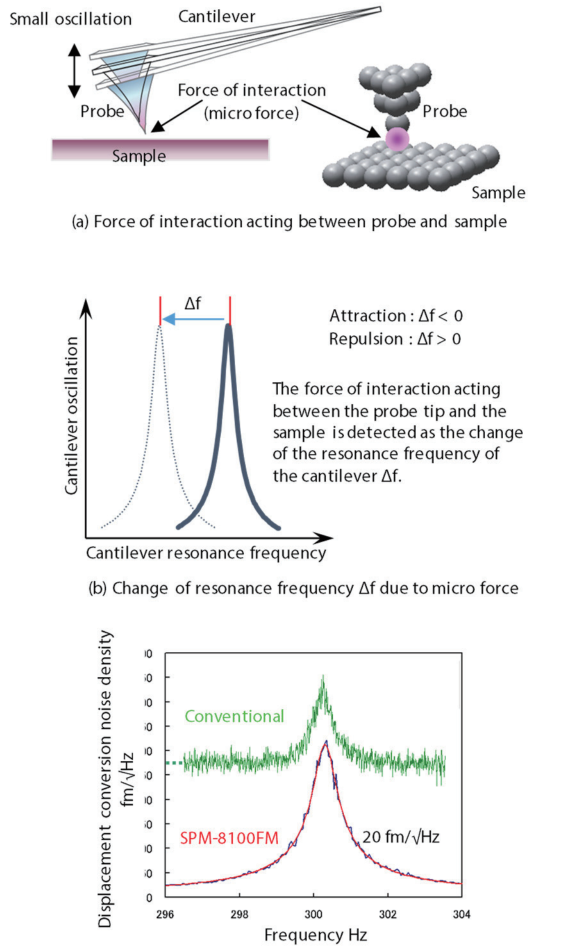


Fig. 5 Schematic Diagram of FM Method

Fig. 6 shows the principle of cross-sectional imaging. The force received by the probe while changing the distance (Z direction) between the probe and the sample is measured as Δf by the force curve method. Cross-sectional imaging of the vicinity of the sample surface is possible by continuously scanning this in the X direction. The intensity of the force received by the probe is expressed by contrast in the image.

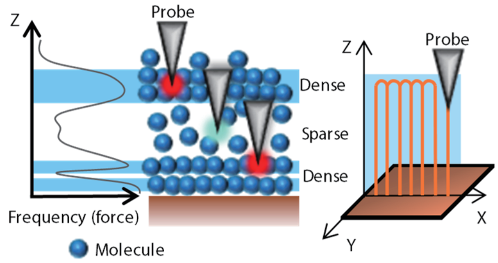
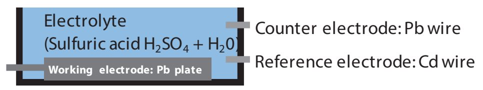


Fig. 6 Principle of Cross-Sectional Imaging

Experimental

Electrochemical solution cell

Fig. 7 shows the electrochemical solution cell prepared for this experiment and the reaction formulas. The Pb plate working electrode, which corresponds to the negative electrode, is placed in a sulfuric acid aqueous solution (dilute sulfuric acid). The counter electrode is a Pb wire, and the reference electrode is a cadmium (Cd) wire. Oxidation (discharging) and reduction (charging) are possible by sweeping the voltage impressed on the Pb plate working electrode.



Charging ⇔ Discharging

Counter electrode : $PbO_2 + 4H + SO_4^{2-} + 2e^- \Leftrightarrow PbSO_4 + 2H_2O$

Negative electrode : $Pb + SO_4^{2-} \Leftrightarrow PbSO_4 + 2e^-$

Fig. 7 Electrochemical Solution Cell and Reaction Formulas

Additive sulfonated lignin [3]

Fig. 8 shows the structure of the sulfonated lignin (lignin) used as an additive. In dilute sulfuric acid, lignin exists as lignin-Pb. Improvement of battery performance as a result of the action of lignin-Pb as a surfactant and ion exchange resin is expected.

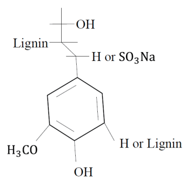


Fig. 8 Structure of Additive Lignin

Two electrolytes were prepared for this experiment, "Only dilute sulfuric acid" and "Sulfuric acid + lignin." Electrochemical solution cells, in which a Pb plate was set, were filled with the respective solutions, and an initial voltage sweep was conducted. Cross-sectional imaging of the interface between the Pb plate and the electrolyte was carried out after the reduction reaction in this sweep.

Reference

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(3) Japan Storage Battery Co., Ltd., "Recent Practical Secondary Batteries – Selection and Use," (1995) pp. 213-2

This report is a revised version of the poster presented at the poster session of the 2018 Academic Lecture Meeting of The Japan Society of Vacuum and Surface Science by Takuhito Watanabe [*1], Nobumitsu Hirai [*2], Akinori Kogure [*3], and Munehiro Kimura [*1].

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