

**The Effect of Additives on Negative Active Materials of Lead-Acid Battery**  
**–An Approach with In-Situ EC-AFM observation–**

Nobumitsu Hirai<sup>1</sup>, Masashi Shiota<sup>1,2</sup>, Toshihiro Tanaka<sup>1</sup>

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

<sup>2</sup>Yuasa Corporation,  
 2-3-31 Kosobe-cho, Takatsuki, Osaka 569-1115, Japan

Lead-acid battery has been widely used for power sources of automotive starters and uninterruptible power supplies all over the world and new applications of this battery to power supply for hybrid cars, load-leveling systems, and so on, have started. It is indispensable to understand the reactions on electrodes of the battery in details during charging or discharging in order to construct an improved battery with suitable performance for each application. In order to improve the battery performance, a lot of additives, so-called “expanders”, such as lignin (lignosulphonate), barium sulfate, carbon black, and so on, are added in negative active materials of the battery [1,2]. However, the detailed mechanism of the effect of additives is still obscure.

Electrochemical atomic force microscopy (EC-AFM), as well as electrochemical scanning tunneling microscopy, is one of powerful tools, by which we can observe in situ the electrode surfaces in electrolytes. Not only atomic or molecular arrangements on single crystals of electrode [3], but also morphology on electrode in a micron scale, can be observed by means of EC-AFM [4]. In this paper, the behavior of Pb electrodes in sulfuric acid solution with additives, such as lignin, barium sulfate, and so on, investigated by EC-AFM, is shown [5, 6].

Figures 1 and 2 show in-situ EC-AFM images (10μm×10μm) on a Pb sheet in electrolytes at –20°C during anodic oxidation, corresponding to the charging of the negative electrode of lead acid battery. These EC-AFM images indicate the precipitation of lead sulfate crystals on lead surface. The electrolytes used are 5M H<sub>2</sub>SO<sub>4</sub> aqueous solution without lignin for Figs. 1 and 5M SO<sub>4</sub> aqueous solution with 20ppm lignin (Vanillex N, Nippon Paper Industries Co.) for Figs. 2. It is found that the size of the lead sulfate crystals in Fig. 2(d) is larger than that in Fig. 1(d). In the solution with lignin, the surface of the Pb sheet is covered by lignin [7], resulting in the decline of the surface energy. It is known that the density of the critical nuclei decreases when the surface energy of the substrate is smaller. If the density of the critical nuclei decreases, each crystal becomes bigger until whole the surface is passivated by the crystals. Figure 3 shows schematic illustrations of the cross section of the electrode surface after oxidation. These explanations practically agree with the obtained EC-AFM images. In the conference, we will also present the electrochemical behaviors of Pb sheets in the solution with other lignin and lignin-like chemicals.

Figures 4 show in-situ EC-AFM images on a Pb sheet, on which a small amount of barium sulfate powder was fixed by pressing, in 5M H<sub>2</sub>SO<sub>4</sub> aqueous solution at room temperature during anodic oxidation. These EC-AFM images indicate the precipitation of lead sulfate crystals on barium surface powder. In the conference, we will also present the electrochemical behaviors of Pb sheets, on which a small amount of other sulfate powder was fixed by pressing.

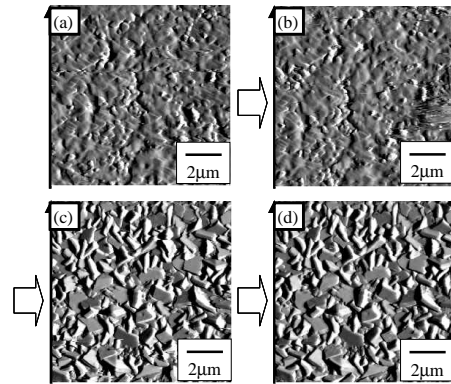


Fig. 1 In-situ EC-AFM images (10μm×10μm) on a Pb sheet in 5M H<sub>2</sub>SO<sub>4</sub> aqueous solution without lignin at –20°C during anodic oxidation.

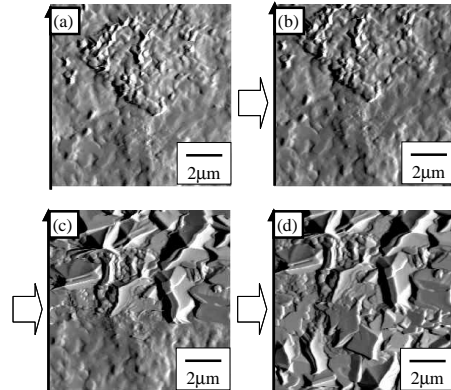


Fig. 2 In-situ EC-AFM images (10μm×10μm) on a Pb sheet in 5M H<sub>2</sub>SO<sub>4</sub> aqueous solution with 20ppm lignin at –20°C during anodic oxidation.

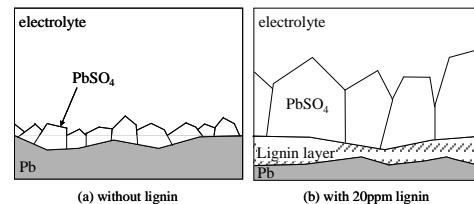


Fig. 3 Schematic illustrations of the cross section of the surface of the Pb sheet after anodic oxidation.

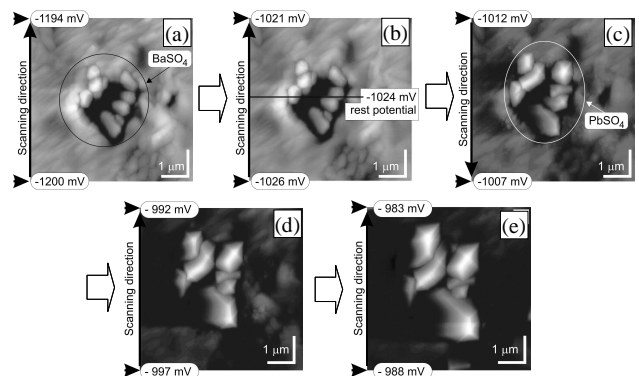


Fig. 4 In-situ EC-AFM images on a Pb sheet, on which a small amount of barium sulfate powder was fixed by pressing, in 5M H<sub>2</sub>SO<sub>4</sub> aqueous solution at room temperature during anodic oxidation.

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