

Reaction between lead oxide and lignin in aqueous solution

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Abstract

The reaction between lignin and the surface oxide layer on Pb plates was studied by dipping experiments in ultra pure water with lignin, anodic polarograms in sulfuric acid solution with or without lignin and also scanning electron microscopy (SEM) observations of the sample surface after anodic polarization. It is found that the lignin reacts with the surface oxide on the Pb plates in ultra pure water with lignin to reaction products containing Pb and the lignin and they grew preferentially at the interface between Pb and the surface oxide. The deposits formed on the surface suppress to passivate the Pb surface under sulfuric acid solution.

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1. Introduction

Lead–acid batteries are widely used for power sources of automotive starters and uninterruptible power supplies (UPS), and the applications to power supplies for hybrid cars and load-leveling systems are widely tried. Various additives, such as carbon, barium sulfate, lignin (organic expander) and so on, are mixed into the negative electrodes of the batteries. Knowledge on the effects of such additives is indispensable to the development for lead–acid batteries [1–5]. We have already succeeded to observe the Pb or PbO₂ surface in sulfuric acid solution as a model of negative electrodes of lead–acid batteries [6–10] or positive ones [11,12], by in situ electrochemical atomic force microscopy (EC-AFM). In these works, it is found that the lignin acts to remove the obstructive layer from the electrode surface by a reductive or solvent effect [9], however, the detailed mechanism is still obscure. On the other hand, it is important to recognize the reaction between lead oxide and lignin, because negative active materials in lead–acid battery are mixture of oxidized Pb powder and various additives. The following experiments were prepared to clarify the reaction between lead oxide and lignin. Firstly, Pb plates covered by the surface oxide were dipped in the pure water containing lignin “without sulfuric acid”, to investigate the reaction be-

tween lead oxide and lignin and reaction products on the Pb surface. We have also investigated the influence of the products on the electrochemical reactions in the usual electrolyte solution “with sulfuric acid” by anodic polarization method and scanning electron microscopy (SEM) observations.

2. Experimental

The samples in 20 mm × 20 mm square were cut out from rolled Pb sheets (Nilaco Co., 99.99%). The thickness was 1 mm and the surface was covered with the oxide layer. The solutions were ultra pure water (>18 MΩ cm in the electric resistance) containing 40 ppm lignin and aqueous solution with 100 mM sulfuric acid (Wako Pure Chemical Industries, Ltd.). The lignin was ‘Vanillex N’ from Nippon Paper Industries Co. The color of the solutions with lignin is brown. All of the experiments were conducted at room temperature under ultra pure water and various solutions without any deaeration.

3. Results and discussion

3.1. Dipping experiments

The samples of the Pb sheets, prepared as follows, were dipped into ultra pure water containing 40 ppm lignin in

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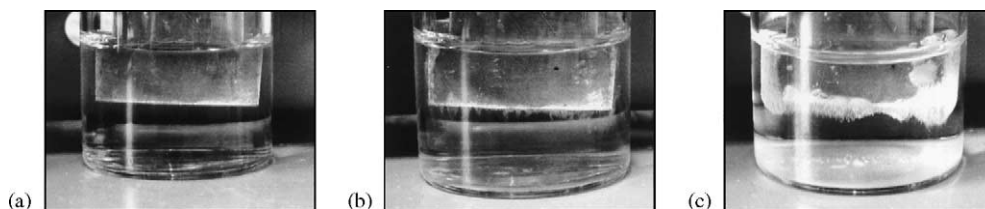


Fig. 1. Change of the surface for Sample 1 after dipped in the solution with 40 ppm lignin for 0 h (a), 8 h (b) and 24 h (c), respectively (Sample 1: covered by the surface oxide layer except the edge).

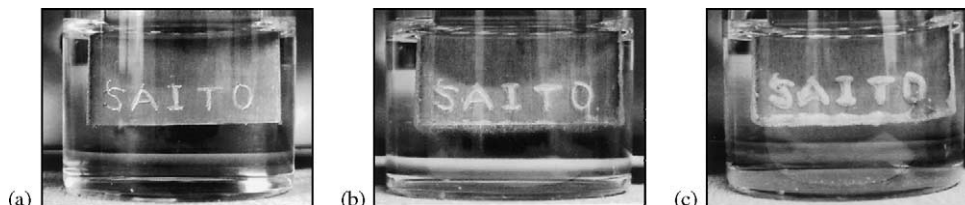


Fig. 2. Change of the surface for Sample 2 after dipped in the solution with 40 ppm lignin for 0 h (a), 8 h (b) and 24 h (c), respectively (Sample 2: bared Pb surface at scratched “SAITO” and the edge).

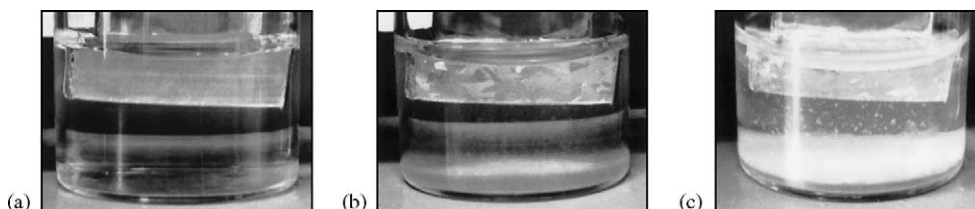


Fig. 3. Change of the surface for Sample 3 after dipped in the solution with 40 ppm lignin for 0 h (a), 8 h (b) and 24 h (c), respectively (Sample 3: washed by acetic acid and ethanol to remove the surface oxide layer).

order to observe the reaction between the sample and lignin. Sample 1 was as-received without pretreatment. Sample 2 was scratched to write a letter “SAITO” on the surface with the glass stick. Sample 3 was washed by acetic acid to remove the surface oxide and then rinsed by ethanol. Figs. 1–3 show the change of the surface morphology for these samples after 0 h (a), 8 h (b), and 24 h (c) dipping in the water containing lignin, respectively. For Sample 1 brown deposits had formed only at the edge after the 8 h dipping. For Sample 2 dipped for more than 8 h, brown deposits could be found both at the edge and at the scratch. Sample 3 had no deposits on the surface, but brown deposits were observed on the bottom of the beaker after the 8 h dipping. After the 24 h dipping for Samples 1 and 2, colors of the solutions changed from brown to colorless, while for Sample 3, the solution changed the color from brown to white and so white deposits were precipitated upon the brown ones.

Since the color changed from brown to colorless after the 24 h dipping of Samples 1 and 2, it was expected that the brown deposits might contain lignin. In order to clarify whether the deposits contain Pb or not, analysis of Pb contents in the solution was performed by means of inductively coupled plasma (ICP) Spectroscopy. For ICP analysis, two solutions containing lignin were prepared; Solution 1 including the deposits formed at the sample edge after the 24 h dipping, and Solution 2 took out the deposits from the solu-

tion after the 24 h dipping. The contents of Pb in Solutions 1 and 2 are shown in Table 1. These results indicate that not only the solution but also the deposit contains Pb ions. This result shows that the surface oxide in contact with bared Pb at the edge reacts with lignin. The similar color change from brown to colorless was also observed after 2 days of addition of lignin–PbO powder mixture into the solution. This result also suggests that the PbO reacts with the lignin. It is known that lignin affects the fluidity and plasticity of the negative paste in lead–acid battery [13]. We consider that lignin also reacts with the negative active materials, which are made from the mixture of the oxidized Pb powders, in the paste, resulting in affecting on the characteristics of the paste.

Secondly, it was examined whether the deposits grow preferentially or not. Since no deposits were observed on the surface for Sample 3 after removal of the surface oxide, the deposits were not grown preferentially on the bare Pb surface. Since the surface of Samples 1 and 2 had no deposits but they observed only on the edge and the scratch. It

Table 1
The contents of Pb in Solutions 1 and 2 by mean of ICP spectroscopy

Solution	Pb contents (ppm)
1	2
7.77	4.77

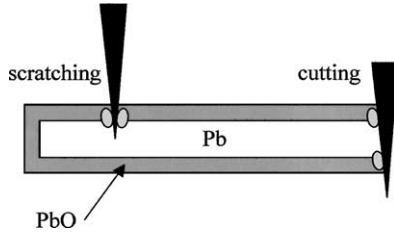


Fig. 4. Schematic illustration of a Pb plate covered by the surface oxide. The interface of Pb and PbO is formed (circle) by scratching or cutting the sample.

suggested that the deposits could not be grown preferentially at the place where only lead oxide exists. Fig. 4 shows the schematic illustration of the samples covered with the oxide layer. The circles in Fig. 4 indicate the interfaces between Pb and lead oxide that was made by cutting or scratching. Brown deposits were formed only at these interfaces, it suggests that the lignin in the solutions reacts with the surface oxide layer on Pb, and formed the compounds containing Pb and the lignin. But the compounds grow preferentially at the interface between Pb and the lead oxide. When the surface oxide on the samples is removed (Sample 3), Pb

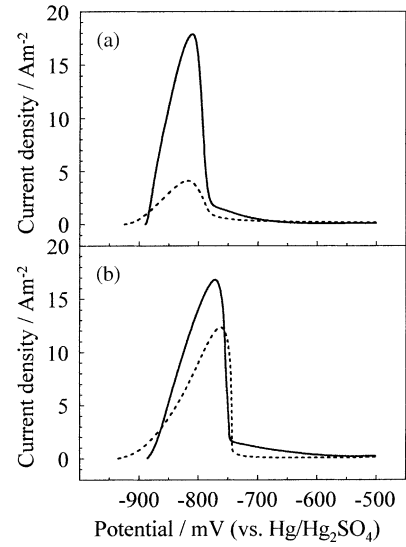


Fig. 6. Anodic polarograms for Sample 3 (solid line) and Sample 4 (dashed line) (Sample 3: washed by acetic acid and ethanol to remove the surface oxide layer; Sample 4: washed in ethanol and covered by the surface oxide layer) (a) is for Procedure A and (b) for Procedure B as shown in Fig. 5.

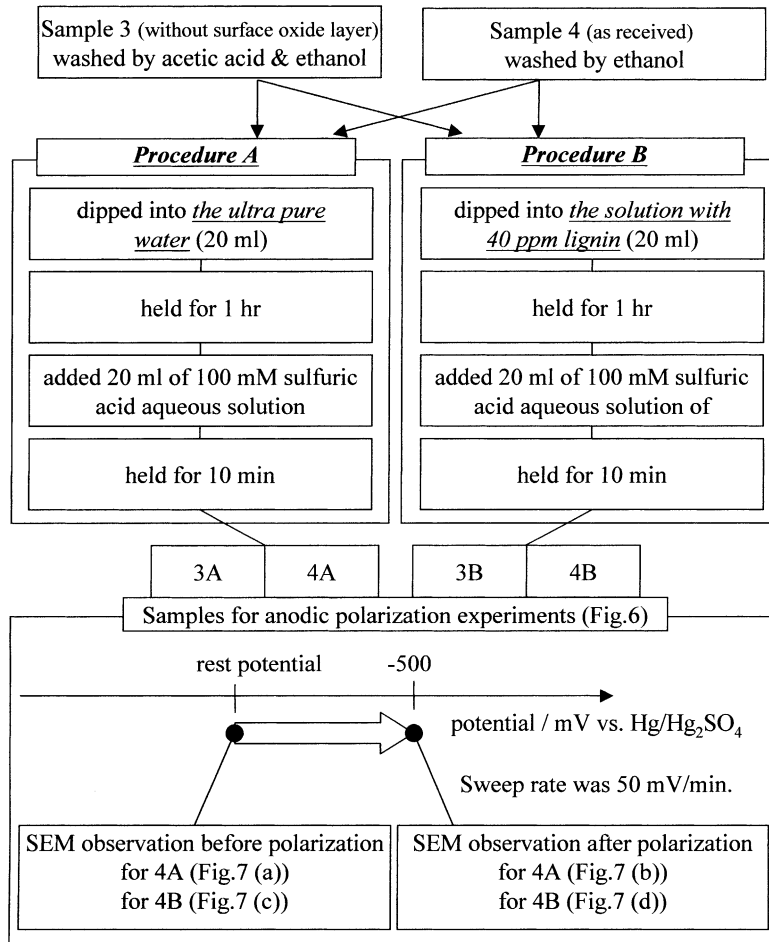


Fig. 5. Experimental procedure for the anodic polarization experiments and SEM observations.

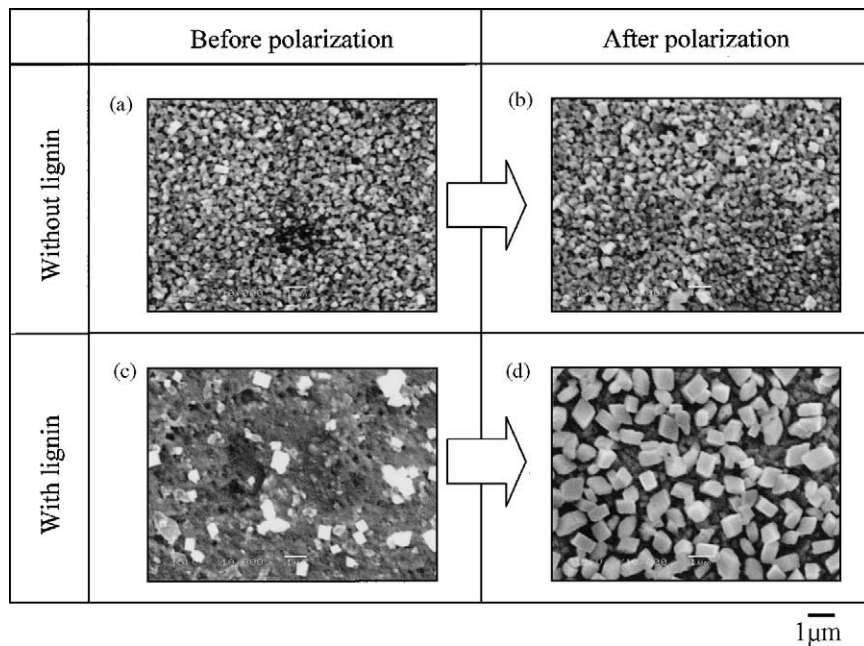


Fig. 7. SEM images for Sample 4 before or after anodic polarization. The detailed experimental procedure is shown in Fig. 5. The image for Procedure A (a) before anodic polarization and (b) after anodic polarization. The image for Procedure B (c) before anodic polarization and (d) after anodic polarization.

will dissolve easily into the solution from the samples. After the Pb^{2+} ions are saturated in the solution, the white $\text{Pb}(\text{OH})_2$ is precipitated. In the case of Sample 3 (Fig. 3), we consider that the brown deposits are reaction products between lignin and $\text{Pb}(\text{OH})_2$. While the white deposits is $\text{Pb}(\text{OH})_2$, which formed after most of the lignin is expired.

3.2. Anodic polarization experiments

The anodic polarization experiments were performed in order to examine the effect of “lead oxide–lignin reaction” on electrochemical behavior in sulfuric acid solution. The electrochemical cell comprised a Pb electrode as the working electrode, a PbO_2 electrode as the counter electrode, and an $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode, to which all potentials are referred. The electrochemical operations were carried out by the potentiostat/galvanostat. The conditions are shown in Fig. 5. The solid and dashed lines in Fig. 6 show the results of anodic polarograms for Samples 3 and 4, respectively. When there was no lignin in the solution (Procedure A), the anodic capacity for Sample 4 was about 20% as compared with that for Sample 3 as shown Fig. 6(a). On the contrary, when there was some lignin in the solution (Procedure B), the anodic capacity of Sample 4 was only about 70% as compared with that of Sample 3 (see Fig. 6(b)). These results allow the following considerations. In the case of Pb plates with the surface oxide (Sample 4), the surface is almost passivated in the ultra pure water by PbSO_4 formation immediately after sulfuric acid is added. However, in the solution with lignin, the passivation of the surface is restrained even if sulfuric acid is added.

3.3. SEM observations

Ex situ scanning electron microscopy observed the formation of PbSO_4 in the solution with or without lignin. Sample 4 is used and the experimental procedure for the imaging is as shown in Fig. 5. Fig. 7(a) and (b) show the SEM images after dipping Sample 4 in the solution without lignin, while Fig. 7(c) and (d) with lignin. Fig. 7(a) and (c), and (b) and (d) show the images before and after the anodic polarization, respectively. In case of no lignin, the surface was almost covered with small crystal of PbSO_4 as shown in Fig. 7(a) and the average size is about 300 nm. After the anodic polarization in the solution without lignin, the PbSO_4 crystals more densely covered the surface as shown in Fig. 7(b). On the contrary, in the solution with lignin, PbSO_4 crystals deposited on the limited part of the surface as shown in Fig. 7(c). After the polarization, those crystals grew up to be larger as shown in Fig. 7(d). From these images, it may conclude that lignin covered the surface of the samples and PbSO_4 crystals grow selectively at limited parts of the surface.

4. Conclusions

We have investigated the reaction between lignin and the surface oxide on Pb plates by means of dipping experiments in the solution “without sulfuric acid” followed by anodic polarization experiments in the solution “with sulfuric acid”, and SEM observations. The experimental results led to the following conclusions.

1. The lignin in the ultra pure water reacts with the surface oxide. The deposits containing Pb and lignin are formed on the Pb plates, and they preferentially grew up at the interface between Pb and the surface oxide.
2. When the Pb samples have the surface oxide layer and no lignin is in the solution, the surface is passivated by PbSO₄ formation, immediately after the sulfuric acid is added. However, when lignin is in the solution, the passivation of the surface is restrained even after the sulfuric acid is added.

In order to innovate on lead–acid batteries, more attention should be paid to “lead oxide–lignin reaction”, since the negative active materials are made from the mixture of the oxidized Pb powders, and the additives including lignin.

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References

- [1] M. Shiomi, T. Funato, K. Nakamura, K. Takahashi, M. Tsubota, J. Power Sources 64 (1997) 147–152.
- [2] D.P. Boden, J. Power Sources 73 (1998) 89–92.
- [3] C. Francia, M. Maja, P. Spinelli, F. Saez, B. Martinez, D. Marin, J. Power Sources 85 (2000) 102–109.
- [4] R. Flores, L.M. Blanco, J. Power Sources 78 (1999) 30–34.
- [5] B. Culpin, D.A.J. Rand, J. Power Sources 36 (1991) 415–438.
- [6] Y. Yamaguchi, M. Shiota, Y. Nakayama, N. Hirai, S. Hara, J. Power Sources 85 (2000) 22–28.
- [7] Y. Yamaguchi, M. Shiota, Y. Nakayama, N. Hirai, S. Hara, J. Power Sources 93 (2001) 104–112.
- [8] Y. Yamaguchi, M. Shiota, Y. Nakayama, M. Hosokawa, N. Hirai, S. Hara, J. Power Sources 102 (2001) 156–162.
- [9] I. Ban, Y. Yamaguchi, Y. Nakayama, N. Hirai, S. Hara, J. Power Sources 107 (2002) 167–172.
- [10] N. Hirai, K. Takeda, S. Hara, M. Shiota, Y. Yamaguchi, Y. Nakayama, J. Power Sources 113 (2003) 329–334.
- [11] M. Shiota, Y. Yamaguchi, Y. Nakayama, K. Adachi, S. Taniguchi, N. Hirai, S. Hara, J. Power Sources 95 (2001) 203–208.
- [12] M. Shiota, Y. Yamaguchi, Y. Nakayama, N. Hirai, S. Hara, J. Power Sources 113 (2003) 277–280.
- [13] D.A.J. Rand, D.P. Boden, C.S. Lakshmi, R.F. Nelson, R.D. Prengaman, J. Power Sources 107 (2002) 280–300.