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Oxidation-resistant Film for Negative Active Materials of Lead–Acid Batteries Generated by Co-adsorption of Ascorbic Acid and Boric Acid

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A simple and useful technique for preparing an oxidation-resistant film on a Pb electrode is reported. By dipping a Pb electrode into a mixed solution of 1% ascorbic and 5% boric acids at 40 °C and then drying in air, the film was coated on the surface to protect the Pb electrode from oxidation. EPMA results clearly showed that no oxidation of the Pb surface took place even after one week in air. In addition, the discharge curve of a Pb plate treated with the reported method was as good as that obtained from conventional methods.

The lead–acid battery, a secondary battery, was invented in 1859 by French physicist Gaston Planté. This type of battery is the oldest type of rechargeable battery and, despite having the second lowest energy-to-weight ratio (next to the nickel–iron battery) and a correspondingly low energy-to-volume ratio, the ability to supply high surge currents means that the cells maintain a relatively large power-to-weight ratio. These features, along with low cost, make such batteries attractive for use in cars to provide the high current required by automobile starter motors.[1]

Although the lead–acid battery has been used for over 50 years, research and development to obtain better performance still continues.[2–5] Oxidation of the Pb electrode is one of the most important problems and results in decreased capacitance of the battery after the first discharge. The charged negative plates of the lead–acid battery (Pb plates) are easily oxidized when they are exposed to air under most conditions. Various methods have been reported to prevent such oxidation on the negative plate. In particular, one method described by the Eagle-Picher Lead Co., which involves the use of superheated steam at 182 to 188 °C for drying, followed by cooling in saturated steam at a lower temperature (SHS method), has been used for a very long time. However, this method has the disadvantages of high cost and limited plate size.[6]

So far we have tried to protect the Pb plate by coating with the boric acid solution, and this method is good for the purpose to some extent. During the improvement of the procedure, we have found an additional component plays an important role for the protection of Pb plate. Here, we report a new method for the prevention of Pb plate oxidation. By dipping the Pb plate, the negative active material (NAM) of the lead–acid battery, into a mixed solution of ascorbic acid and boric acid, oxidation of the electrode surface was prevented for several weeks.

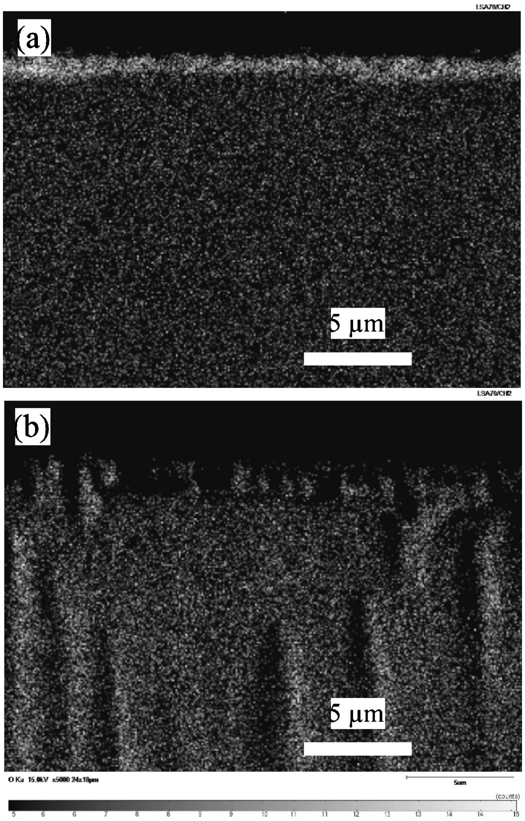

Figure 1. O maps of the Pb plates (20 μm depth × 25 μm width) analyzed by the EPMA after 7 days in air. The reduced electrodes were treated in (a) pure water and (b) a mixed solution of 1% (w/w) ascorbic acid and 5% (w/w) boric acid at 40 °C for 10 min.

A Pb plate (99.999%) was purchased from Nilaco Co., Ltd. Ascorbic acid and boric acid were purchased from Waco Chemicals and were used as received. The electrode (10 mm square) was polished with emery paper (#400) and soaked in a dilute acetic acid solution followed by immersion in the mixed solution of ascorbic acid and boric acid. The cross-sectional area of the Pb plate was observed by an electron probe microanalyzer (EMPA-1720, Shimadzu, Japan). Before EPMA experiment the cross sectional area of the sample was treated with an ion milling machine (Hitachi Ion Milling 3500). Discharge experiments were carried out in 3 M H_2SO_4.

Figure 1 shows O maps of the Pb plates (20 μm depth × 25 μm width) analyzed by the EPMA after 7 days in air. When the polished and reduced Pb electrode was treated in pure water, the EPMA map shown in Figure 1a was acquired. In contrast, when the Pb electrode was treated with a 1% (w/w) ascorbic acid and 5% (w/w) boric acid solution at 40 °C for 10 min (hereafter, we call this treatment the AB method), the EPMA map shown in Figure 1b was obtained. Since the cross-sectional area of the electrode was cleaned and flattened by the ion milling for ca. 16 h, the surface was oxidized to some extent.

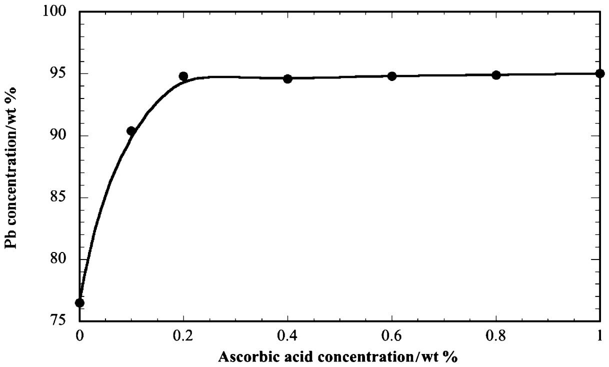

Figure 2. Effect of ascorbic acid concentration in the mixed solution used for the AB method on the Pb concentration.

In the O map (a), the relatively high concentration of the oxygen layer was clearly observed at the electrode surface. This result indicated that the surface of the electrode exposed to the air was easily oxidized and that the oxide layer (PbO or PbO_2) was formed. In this experiment, we used pure Pb plates (nonporous) with a thickness of 1 mm, and the oxygen-rich layer extended to about 2 µm in depth. As of the time of publication, we have not checked the rate of formation of the oxidized Pb, but the oxidation of Pb was easily confirmed.

In contrast, when the Pb plate was treated with the AB method, no oxidized layers were seen in the O map (b), and the amount of oxygen was very low over the observed region. Therefore, the mild surface treatment of the AB method protected the Pb surface from oxidation. In addition, when the Pb plate was treated with only 5% boric acid at 40 °C, the oxygen layer (PbO or PbO_2) was clearly seen, although the thickness of the layer was thinner than that seen in image (a). Additionally, when the Pb was treated with 1% ascorbic acid only, the oxidized layer was clearly observed (data not shown).

To investigate the effect of ascorbic acid on the protection of the Pb plate, the Pb plate was treated with several mixed solutions with varying ascorbic acid content and constant 5% boric acid. The amount of Pb was then evaluated using quantitative analysis. Figure 2 shows the effect of the concentration of ascorbic acid (wt %) on the concentration of the Pb (wt %). The powdered NAM was treated with 1 mM acetic acid to remove PbO and $PbSO_4$ contained in the NAM as an impurity. The remaining Pb metal was weighed, and the concentration of Pb was obtained. When the Pb plate was treated with boric acid only (0% ascorbic acid), the Pb concentration was relatively low. The Pb concentration then increased with increases in the concentration of ascorbic acid. The maximum Pb concentration of 95% was seen in the case where the plate was treated with a solution of 0.6% ascorbic acid and 5% boric acid. Furthermore, when the Pb plate was treated using the SHS method, the observed Pb concentration was 95.2%; thus, the AB method was nearly identical to the SHS method. As of the time of publication, we are in the process of obtaining information about co-adsorbed ascorbic acid and boric acid molecules on the Pb surface.

Figure 3 shows the discharge curves of the lead–acid battery (six cells in series) using the NAM treated with the AB method (closed circle) and the SHS method (open square). Here the electrolyte used for the experiments was sulfuric acid with a specific gravity of 1.28 g cm^{-3}. For discharge curve data collection, the electrolyte was added to the cell immediately before measurement. The Pb plates treated using the AB method and the SHS method were then exposed to air for 7 days. We found that the terminal voltage decreased with increases in the discharge time. Furthermore, the curve obtained using the AB-treated NAM was very similar to that of the SHS-treated NAM. This result shows that no special effects on the discharge of the battery were caused by the AB method. When the NAM prepared without the AB method was analyzed, the cell voltage decreased rapidly and reached a final cell voltage (6 V) within 50 s. These results further indicate that the AB method was effective for retaining capacity even when the NAM was exposed to air.

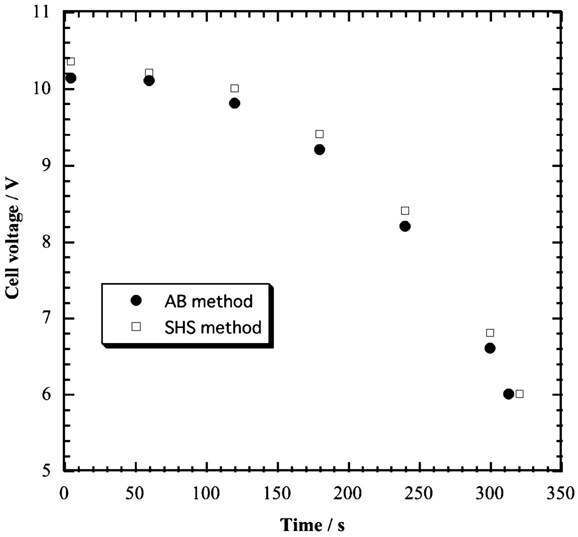

Figure 3. Discharge curves of a lead–acid battery using the NAM treated with the AB (closed circles) and SHS methods (open squares). Discharge current: 150 A. The temperature of the battery was 25 °C. The specific gravity of the sulfuric acid was 1.28 g cm^{-3}.

In conclusion, we have reported a new, simple method to protect the NAM of lead–acid batteries from oxidation by dipping the Pb plate into a mixed solution of ascorbic acid and boric acid. This method could be applied to large-scale protection against oxidation in lead–acid batteries in the future.

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