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Journal of Power Sources 95 (2001) 125–129

JOURNAL OF POWER SOURCES

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# Development of positive electrodes with an $SnO_2$ coating by applying a sputtering technique for lead-acid batteries

Isamu Kurisawa*, Masaaki Shiomi, Shigeharu Ohsumi,
Masashi Iwata, Masaharu Tsubota

*Battery Development Center, Japan Storage Battery Co. Ltd., Nishinosho, Kisshoin, Minami-ku, Kyoto, Japan*

**Abstract**

In order to prevent positive grid corrosion and to obtain a long life for positive electrodes of lead-acid batteries, a conductive and corrosion resistant $SnO_2$ (tin dioxide) layer was formed on a Ti (titanium) substrate by a conventional dip-coating method. However, it is impossible to apply this method to a Pb (lead) substrate, because the dip-coating method needs a calcination process, at a temperature higher (conventionally from 450 to 600°C) than the melting point of Pb ($T_m$: 327°C).

For this reason, an $SnO_2$ layer to protect the substrate against passivation and/or corrosion was formed on Ti and/or Pb electrodes by applying sputtering, a method which is often used in the production of semiconductors.

This improved electrode, with an $SnO_2$ layer, was not corroded at all, even though the thickness of the $SnO_2$ layer was only about 15 μm.

The biggest problem of the $SnO_2$ layer is that it dissolves in sulfuric acid when the positive electrode is polarized below 0.5 V (versus Pb/$PbSO_4$). This suggests that this electrode should not be subjected to deep discharge. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Lead-acid batteries; Positive electrode; Corrosion; Tin dioxide; Sputtering

## 1. Introduction

The demand for longer life and higher reliability of batteries in telecommunication in, photovoltaic application and in RAPS (remote area power supply) systems continues to increase.

Usually positive grid corrosion is one of the major failure modes of VRLA (valve regulated lead-acid) batteries for these applications. Therefore, a lot of attempts have been made to reduce corrosion of positive grids by adding alloying elements, by heat treatment, and so on.

Formation of ceramic materials such as $SnO_2$ and $RuO_2$ on the surface of positive electrodes has also been studied in attempts to prevent corrosion [1,2]. In those studies, the $SnO_2$ layer was formed on a Ti substrate and/or a glass sheet (but not on Pb or Pb alloy grids), by a dip-coating method. The dip-coating method needs a calcination process at a temperature higher (conventionally 450–600°C) than the melting point of Pb ($T_m$: 327°C), resulting in a much higher material cost of positive electrodes than those of conventional VRLA batteries.

In order to form an $SnO_2$ layer for corrosion protection of a Pb electrode, its formation temperature must be lower than about 300°C. Therefore, we applied a sputtering technique, as used in semiconductor production, and tried to develop a new type of positive electrode which is not expensive and has good corrosion resistance.

In this report, the results of both corrosion test and the charge–discharge cycling tests of Ti or Pb/$SnO_2$/PAM (positive active mass) electrodes are shown.

## 2. Experimental and results

### 2.1. Formation of $SnO_2$ layer by sputtering

An $SnO_2$ layer was formed on Ti or Pb substrate by sputtering as follows:

- Substrate: Ti, Pb ($24\,mm^W \times 20\,mm^H \times 0.5\,mm^T$).
- Sputtering rate: 0.4 μm/h.
- Substrate temperature: 120°C.
- Target: $SnO_2$ sintered compact.
- Sputtering gas: $6 \times 10^{-3}$ Torr (Ar).
- Equipment: magnetron sputtering.

Substrates were degreased by an ultrasonic cleaning in ethanol before sputtering. The thickness of the $SnO_2$ layer was adjusted by changing sputtering time. The substrates were rotated slowly during sputtering in order to get a homogenous deposition of $SnO_2$.

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* Corresponding author. Tel.: +81-75-316-3104; fax: +81-75-316-3798.
*E-mail address*: isamu_kurisawa@gs.nippondenchi.co.jp (I. Kurisawa).

PII: S0378-7753(00)00641-8

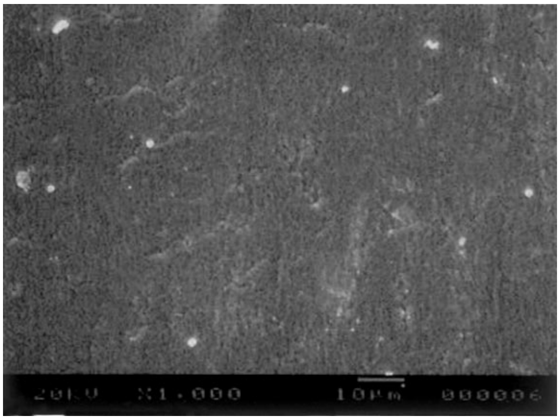


Fig. 1. SEM micrograph of $SnO_2$ layer formed by sputtering.

The surface condition of deposited $SnO_2$ was observed by SEM and the crystal structure of the $SnO_2$ was analyzed by XRD. The surface condition of the $SnO_2$ layer formed by sputtering was very smooth as shown in Fig. 1, and the deposited material was confirmed as $SnO_2$ by XRD. In addition, the electric conductance of the $SnO_2$ layer was measured. It had a conductivity of about 0.1 $\Omega^{-1}\,cm^{-1}$ when the thickness of $SnO_2$ layer was 15 µm.

### 2.2. Electrochemical characteristics of the $SnO_2$ layer deposited by sputtering as a positive electrode

#### 2.2.1. Linear sweep voltammetry (LSV)

First, a linear sweep voltammetry of Pb and Pb/$SnO_2$(1 $\mu m^T$) was carried out over a wide potential range. A photograph and a drawing of an experimental cell are shown in Figs. 2 and 3, respectively. Electrolyte leakage was prevented by pressing a cell (1) against a cell (2) through a rubber sheet. The effective area of the working electrode exposed to the electrolyte was 1 $cm^2$.

| Electrode | Sweep range/V vs. Pb/$PbSO_4$ | Number of sweep |
|---|---|---|
| (a) Pb | 1.0–2.7 | 50 |
| (b) Pb/$SnO_2$ (1 $\mu m^T$) | 1.0–3.0 | 50 |
| (c) Pb/$SnO_2$ (1 $\mu m^T$) | 0.2–2.7 | 1 after (b) |

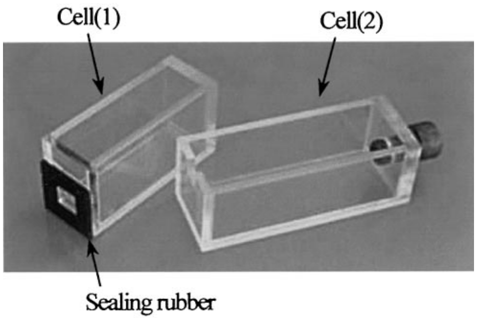


Fig. 2. Photo of experimental cell.

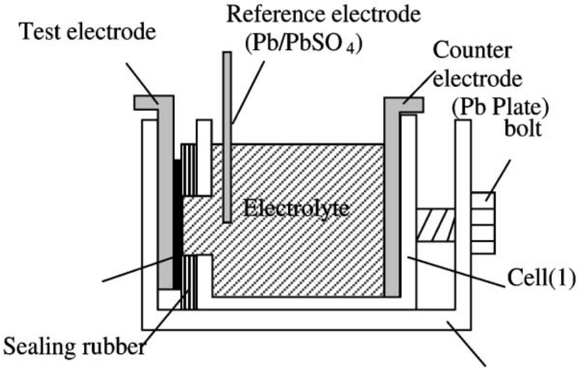


Fig. 3. Drawing of experimental cell.

- Substrate: Pb (20 $mm^W$ × 20 $mm^H$ × 0.5 $mm^T$).
- Counter electrode: Pb plate.
- Reference electrode: Pb/$PbSO_4$.
- Electrolyte: s.g. 1.280 (20°C) $H_2SO_4$.
- Sweep rate: 10 mV/s.

Until the 50th cycle, these electrodes were cycled in the potential range from 1.0 to 2.7 V (versus Pb/$PbSO_4$). The curves a and b of Fig. 4 show LSV characteristics at the 50th cycle of Pb and Pb/$SnO_2$ electrodes, respectively. A small current peak (arrow A) of the $PbSO_4$ formation reaction from $PbO_2$ was observed at about 2.0 V (versus Pb/$PbSO_4$) on Pb/$SnO_2$ electrode, which indicated the existence of pinholes in the thin $SnO_2$ layer.

At the 51st cycle, the Pb/$SnO_2$ electrode was polarized to 0.2 V (versus Pb/$PbSO_4$). A small cathodic current (arrow B) was observed below 0.5 V (versus Pb/$PbSO_4$) as shown in curve c. This may be due to the dissolution of $SnO_2$ into the sulfuric acid.

Fig. 5 shows photos of the test electrodes after LSV of electrode (b) after 50 cycles and electrode (c) after 51 cycles. It was found that part of the $SnO_2$ layer on electrode (c) disappeared. This indicates that the $SnO_2$ layer was dissolved into the sulfuric acid solution when $SnO_2$ was

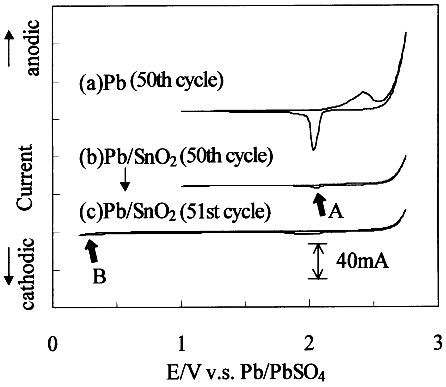
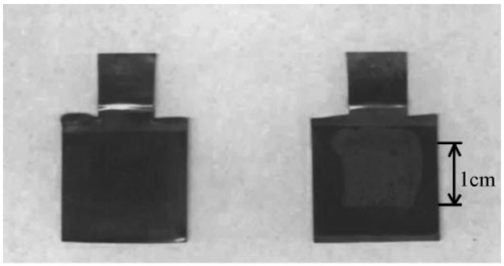


Fig. 4. Current–potential curve of Pb and Pb/$SnO_2$ electrodes.



Electrode (b) after 50 cycles Electrode (c) after 51 cycles

Fig. 5. Test electrodes after LSV.

polarized below 0.5 V (versus $Pb/PbSO_4$), suggesting that this electrode should not be subjected to deep discharge.

### *2.2.2. Anodic oxidation test (1)*

The thickness of the $SnO_2$ layer which has no pin-hole, was studied by using a Ti substrate, because Ti is easily passivated and causes a large internal resistance when Ti contacts with sulfuric acid solution.

First, $SnO_2$ layers of various thicknesses were formed by a sputtering on the surface of Ti substrates. Next, conventional PAM paste was applied on the $Ti/SnO_2$ substrates, and then the test cell was constructed as shown in Fig. 6. To keep the constant contact between PAM and the substrates, a weight of 2 kg was put on the negative plate. Container formation was carried out under the following conditions. The most important point was to start the formation as soon as possible after the electrolyte filling of the cell, because the potential of the unformed positive plates was lower than 0.5 V (versus $Pb/PbSO_4$) and the $SnO_2$ layer on the substrate might dissolve into the electrolyte before the formation started.

- Test electrode: $Ti/SnO_2/PAM$, Pb/PAM.
- PAM tablet: $20\,mm^W \times 24\,mm^L \times 0.6\,mm^T$ (1.3 g).
- Thickness of $SnO_2$ layer: 0.3, 4.8, 8, 12 μm.
- Counter electrode: pasted negative plate.
- Reference electrode: $Pb/PbSO_4$.
- Electrolyte: s.g. 1.280 (20°C) $H_2SO_4$.
- Formation current: 12 mA.
- Formation time: 48 h.
- Temperature: 20–25°C.

These cells were discharged at 100 mA, and the potential changes of the positive electrode during discharge were measured against a $Pb/PbSO_4$ reference electrode. The discharge curves and the potential drops during the first 2 min are shown in Figs. 7 and 8, respectively. It was found that a thickness of 8 μm and more was necessary in order not to cause the passivation of the Ti substrate. It seems that there are practically no pin-holes in the $SnO_2$ layer with more than 8 μm thickness.

### *2.2.3. Anodic oxidation test (2)*

In order to study the corrosion resistant characteristics of the $SnO_2$ layer, an anodic oxidation test at a constant current was carried out for $Pb/SnO_2/PAM$ electrodes. The structure of the experimental cell is shown in Fig. 9. The cells are the

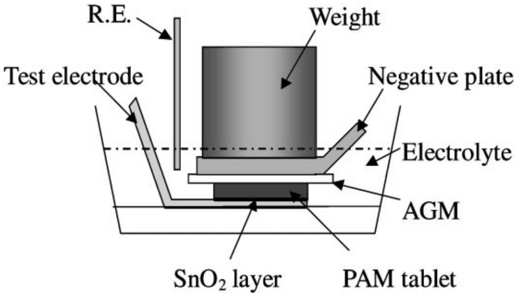


Fig. 6. Experimental cell.

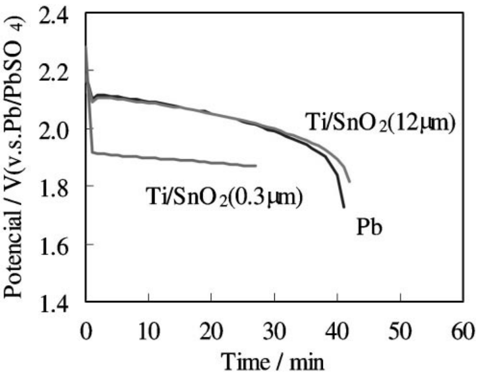


Fig. 7. Discharge characteristics of $Ti/SnO_2/PAM$.

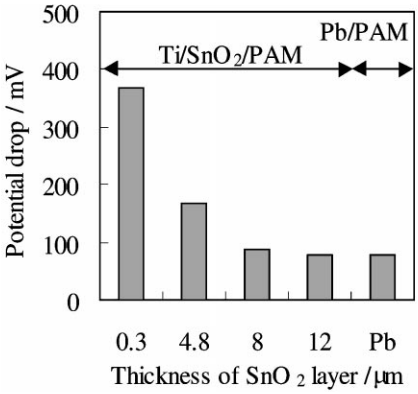


Fig. 8. Relationship between the potential drops during the first 2 min and the thickness of $SnO_2$ layer.

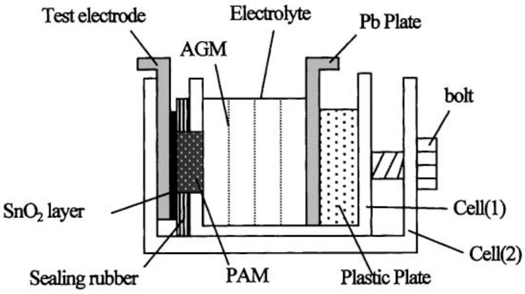


Fig. 9. Experimental cell.

same as shown in Fig. 2. Conventional PAM paste was applied and the plate formation was also carried out soon after the electrolyte filling. The PAM was highly compressed by the AGM separator to prevent shedding of PAM.

The test electrode was overcharged at 20 mA for 600 h at 25°C.

- Test electrode: Pb/$SnO_2$/PAM, Pb/PAM.
- PAM: $10\,mm^W \times 10\,mm^H \times 4\,mm^T$ (6 g).
- $SnO_2$ layer: $20\,mm^W \times 20\,mm^H \times 15\,\mu m^T$ (one side on Pb substrate).
- Counter electrode: Pb plate.
- Electrolyte: s.g. 1.280 (20°C) $H_2SO_4$.
- Formation current: 40 mA.
- Formation time: 64 h.
- Anodic current: 20 mA.
- Anodic time: 600 h.

After the test, the cells were disassembled and the corrosion conditions were observed. Furthermore, the distribution of Sn was observed by EPMA as shown in Fig. 10. The Pb substrate was not corroded at all for the positive plate with an $SnO_2$ coating, while it was heavily corroded for the positive plate without it. $SnO_2$ was confirmed to exist between the Pb substrate and the PAM on Pb/$SnO_2$/PAM electrode, even after the corrosion test. These results show that it had an outstanding effect for suppressing corrosion of the Pb electrode.

### 2.2.4. *Cycle life test with PAM*

From the above test results, it is clear that the corrosion resistant characteristics of the $SnO_2$ layer deposited by sputtering in an anodic oxidation test are excellent. Therefore, a cycling test was carried out to evaluate the durability of $SnO_2$ layer.

In this test, a Ti substrate was used. The experimental cell was the same as shown in Fig. 6, in which a preformed PAM tablet was prepared and was put on the substrate. The Ti/$SnO_2$/PAM electrode was cycled under the following conditions.

DoD was about 65% and the amount of charge was 137% of the previous discharge.

- Test electrode: Ti/$SnO_2$/PAM.
- PAM tablet: $25\,mm^{\phi} \times 3.5\,mm^T$ (7 g).
- Thickness of $SnO_2$ layer: 15 μm (one side on Ti substrate).
- Counter electrode: Pasted negative plate.
- Reference electrode: Pb/$PbSO_4$.
- Electrolyte: s.g. 1.280 (20°C) $H_2SO_4$.
- Discharge: 150 mA × 1 h.
- Charge: 50 mA × 4.1 h.
- Number of cycles: 100.
- Temperature: 20–25°C.
- Capacity test: 150 mA, F.V.: 1.75 V.

Fig. 11 shows a part of the charge–discharge characteristics of the experimental cell during the cycling test. Positive electrode potential varied from 2.0 to 2.5 V (versus Pb/$PbSO_4$) during this test.

The change of discharge capacitiy during this cycling test is shown in Fig. 12. It can be seen that the discharge capacity of a positive plate with an $SnO_2$ layer increased as the

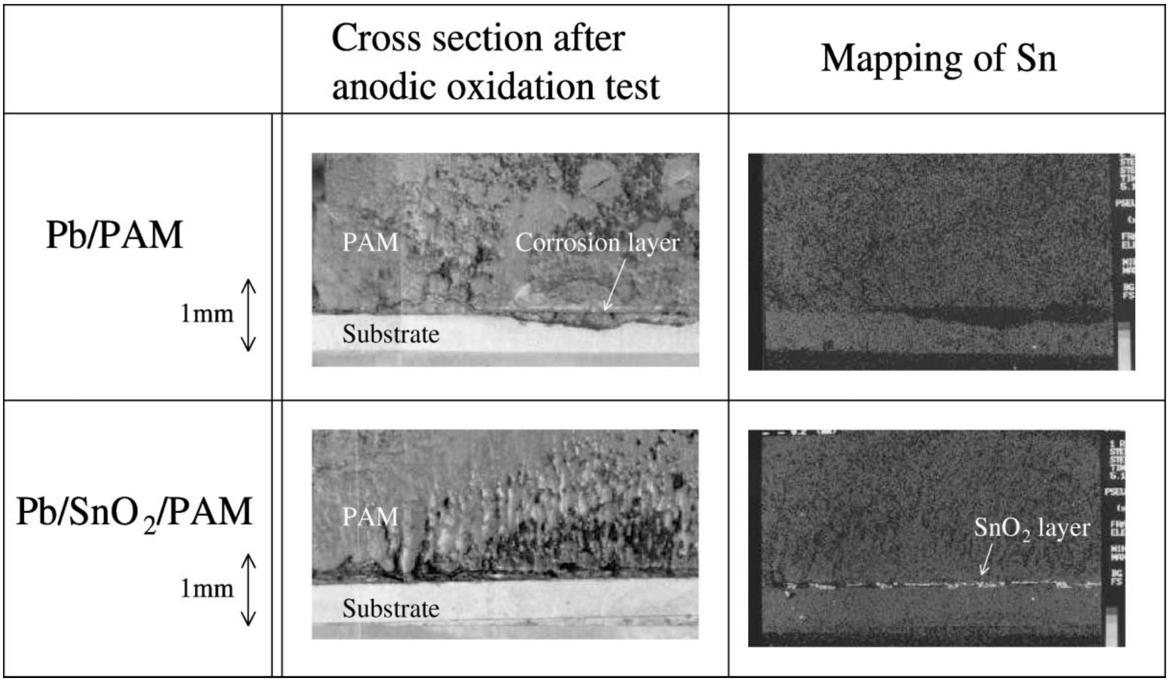


Fig. 10. Cross section of test electrodes with and without $SnO_2$ after anodic oxidation test.

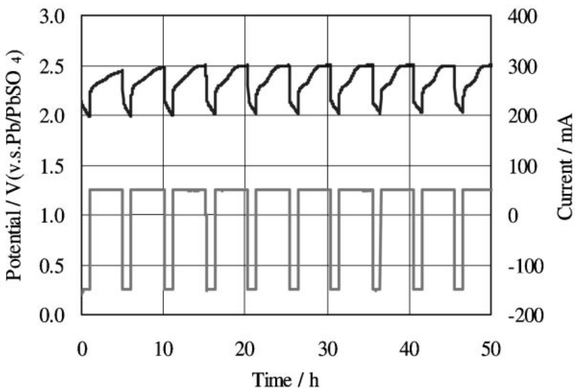


Fig. 11. The charge–discharge characteristics of the Ti/$SnO_2$/PAM plate.

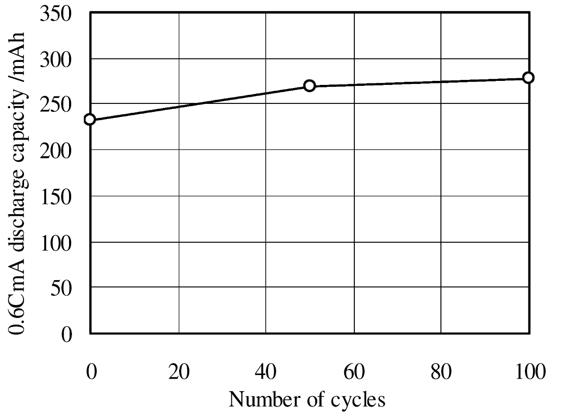


Fig. 12. The change of discharge capacity during the cycling test of the Ti/$SnO_2$/PAM plate.

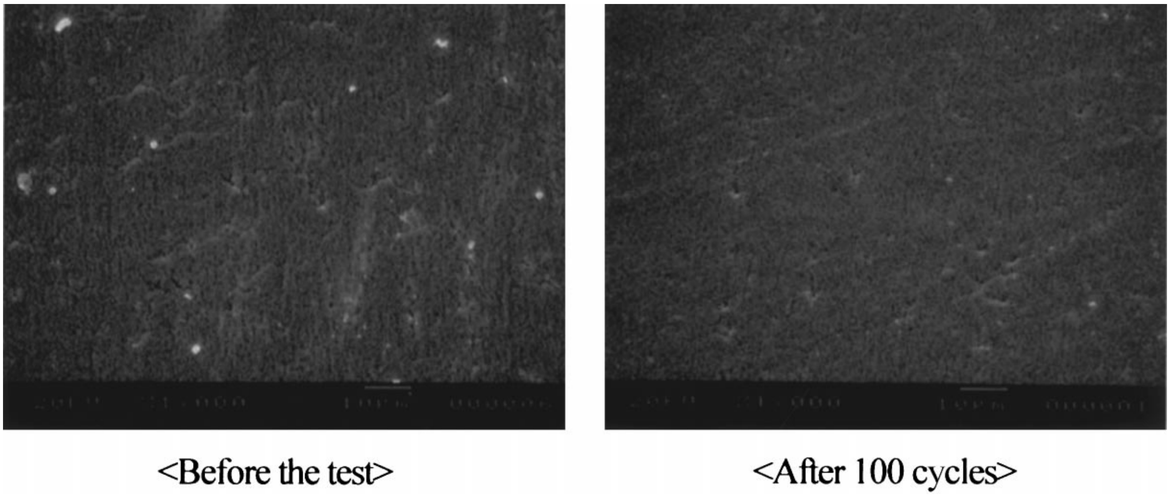

<Before the test> <After 100 cycles>

Fig. 13. SEM micrographs of the $SnO_2$ layer on a Ti substrate.

number of cycles proceeded and no decrease was observed at all.

After 100 cycles, the cell was disassembled and the surface condition of the $SnO_2$ layer was observed by SEM. It was not changed at all compared with the one before the test as shown in Fig. 13.

These results indicate that the $SnO_2$ layer formed by sputtering has a significant corrosion resistance even under a charge–discharge cycling test condition, provided that it is not subjected to a deep discharge to a potential below 0.5 V (versus Pb/$PbSO_4$).

## 3. Conclusions

A thin $SnO_2$ layer formed on a Pb substrate by sputtering was able to improve the corrosion resistance of Pb electrode significantly, although it had a tendency to dissolve into sulfuric acid when overdischarged below about 0.5 V (versus Pb/$PbSO_4$).

A corrosion resistant $SnO_2$ layer formed by sputtering will become one of the key technologies for high reliability and/or long life VRLA batteries. Application tests for SLI, telecommunication, RAPS, and photovoltaic applications will be carried out in the near future.

## Acknowledgements

This study was carried out in the Project of ‘‘Research and Development of Highly Reliable Storage Batteries for Photovoltaic Power Generation Systems’’ supported by NEDO (New Energy and Industrial Technology Development Organization).

## References

[1] C. Iwakura, K. Sakamoto, J. Electrochem. Soc. 132 (10) (1985) 2420–2423.

[2] A.I. Attia, J.J. Rowlette, in: Proceedings of 33rd Power Sources Symposium, 1988, pp. 624–632.