Anodic Durability of DSA-Type Positive Grids for Lead-Acid Batteries*

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The anodic durability of DSA-type positive grids for lead-acid batteries was investigated, using RuO_2 , PdO_x , Sb-doped SnO_2 , IrO_2 , PtO_x and AuO_x as the oxide layer. It was found that a Sb-doped SnO_2 layer is very adhesive to both the titanium base and $\beta\text{-PbO}_2$ layer, and that the addition of oxides having the rutile-type structure and metallic conductivity, such as IrO_2 and RuO_2 , in the Sb-doped SnO_2 layer is very effective for increasing the anodic durability of the $\text{Ti/SnO}_2\text{-SbO}_x/\beta\text{-PbO}_2$ positive grid for lead-acid batteries.

1 Introduction

In our previous works¹⁻³⁾, DSA-type electrodes have been applied to a positive grid in lead-acid batteries, and the DSA-type grids having the long service life and low self-discharge rate have been developed by surface treatments, such as sandblasting and chemical etching, of the titanium base. The performance of the latest $\text{Ti(ce)/RuO}_2/\beta\text{-PbO}_2$ grid is superior to that of the pure Pb grid³⁾. For practical use, however, the service life of the DSA-type plate must be further improved at least up to the clad type plate using the Pb-Sb alloy grid. If the amount of RuO_2 loadings on the titanium base is increased in order to improve the anodic durability of the DSA-type grid, the decrease in discharging efficiency as well as the increase in self-discharge rate of the plate would occur because of the low oxygen overvoltage of the RuO_2 layer, as pointed out previously^{1,2)}. Therefore, another approach to solve the problem is that the RuO_2 layer is replaced by other oxides favorably having the same crystal structure (rutile-type) but higher oxygen overvoltage. In this work, in addition to rutile-type RuO_2 , IrO_2 , SnO_2 and $\beta\text{-PbO}_2$, some oxides of metals such as Pd, Pt and Au were chosen as an intermediate layer coated on the titanium base

of DSA-type grids because they are well known to have the high oxygen overvoltage and to be considerably stable against anodization in sulphuric acid solution.

2 Experimental

The surface of the titanium base was pretreated by mechanical polishing and chemical etching, and hereinafter the pretreated titanium bases will be referred to as Ti(mp) and Ti(ce) , respectively. DSA-type grids were prepared by thermal decomposition method, using aqueous solutions of RuCl_3 , PdCl_2 , SnCl_4 (SbCl_3), IrCl_3 , H_2PtCl_6 and H_2AuCl_4 as a coating solution on the titanium base. The amount of oxide loadings will be indicated in parentheses in mol of metal/ cm^2 . In some cases, $\beta\text{-PbO}_2$ layer (5×10^{-3} mol of metal/ cm^2) was further electrodeposited on the Ti/MO_x surface to prepare the $\text{Ti/MO}_x/\beta\text{-PbO}_2$ grid. The other experimental procedures, including the electrochemical measurement, were completely the same as described in the previous papers^{2,3)}.

3 Results and Discussion

3.1 Anodic durability of $\text{Ti}/\beta\text{-PbO}_2$ grids

The anodic durability of the $\text{Ti}/\beta\text{-PbO}_2$ grids was examined in view of the bond-strength (adhesion) of metal-oxide ($\text{Ti}/\beta\text{-PbO}_2$) and oxide-oxide ($\text{TiO}_2/\beta\text{-PbO}_2$) interfaces. For this experiment, the titanium was chemically etched, and then thermally treated at 450°C in air for several minutes. Figure 1 shows the variation of potential with anodization time at

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Fig. 1 Variation of potential with anodization time for Ti(ce)/ β -PbO₂ grids

Time of heat treatment (450°C) of Ti base
a) 0 min, b) 0.5 min, c) 1 min, d) 2 min

100 mA/cm² for the Ti(ce)/ β -PbO₂ grid. The potentials of grids (a) and (b) were rapidly raised owing to the passivation of the titanium base. On the other hand, the grid (c) whose titanium base was covered with proper amount of the thermally formed TiO₂ layer revealed the longest anodic durability of all grids examined. However, the grid (d) covered with large amount of the TiO₂ layer showed the more anodic potential than grid (c) did because of the additional ohmic resistance of TiO₂ layer. Thus, the interface of the grids can be divided into two groups: Ti-thin TiO₂/ β -PbO₂ and Ti-thick TiO₂/ β -PbO₂. At the latter interface, the mixed crystals or solid solutions may be easily formed since both oxides have the same crystal structure. Such formation of mixed crystals leads to the strong adhesion to each other. It can, therefore, be presumed that the oxide-oxide interface is superior to the metal-oxide interface for the anodic durability.

3.2 Anodic durability of Ti/MO_x grids

The variations of potential with anodization time at 10 mA/cm² for various Ti/MO_x grids are shown in Fig. 2. The anodic durability of the Ti/RuO₂ and Ti/PtO_x grids was determined to be 15 and 125 h, respectively. In the case of the Ti/AuO_x and Ti/PdO_x grids, however, the passivation of the titanium base occurred immediately after the current started to flow. It was found from the X-ray diffraction data that the MO_x layers to these grids except for

Fig. 2 Variation of potential with anodization time for Ti(mp)/MO_x(10⁻²) grids

a) Ti/PdO_x, b) Ti/AuO_x, c) Ti/RuO₂,
d) Ti/PtO_x

Ti/RuO₂ consisted of the mixture of oxide and metal and, in particular, AuO_x and PtO_x were mainly composed of each metal. It is known that TiO₂ formed on titanium metal by heat treatment at 450°C is anatase, in general. But, some workers⁴⁻⁶⁾ have clarified from the X-ray analyses that mixed crystals of TiO₂ with RuO₂ having the rutile structure can be formed by thermal decomposition of mixtures of TiCl₃ (TiCl₄) and RuCl₃, even at 450°C. The difference of the formation ability of mixed crystals among various oxides is probably related to the difference in dimension of the crystal lattice and in volume of the unit cell of oxide. The formation of the mixed crystals of TiO₂ and MO_x was the most important factor for providing the good adhesion between the titanium base and MO_x. The difference of the anodic durability of grids observed in Fig. 2 could be explained on the basis of the difference in the formation ability of mixed crystals at the grid interface: In the case of the Ti/AuO_x and Ti/PdO_x grids, the adhesion between the titanium base and MO_x was relatively weak and the potential of these grids under the anodization was high because TiO₂ and MO_x existed independently at the interface without the formation of mixed crystals. On the other hand, in the case of the Ti/RuO₂ and Ti/PtO_x grids, the adhesion between the titanium base and MO_x was relatively strong because the mixed crystals of rutile-type TiO₂-RuO₂ and TiO₂- β -PtO₂

were formed at the grid interfaces. The mixed crystal layer of TiO_2 - β - PtO_2 was estimated to be thinner than that of RuO_2 because in the former case the main component of the MO_x layer is metallic Pt but not β - PtO_2 . Nevertheless, the Ti/PtO_x grid showed very long service life, compared with the Ti/RuO_2 grid. This result indicates that the anodic durability of grids is determined not only by the formation ability of mixed crystals but also the permeability of oxygen species through the MO_x layer. In general, MO_x layer has the permeability of oxygen species because of its property of self-diffusion of O^{2-} ion, as has been reported by Kavanov *et al.*¹⁷ for the permeability of oxygen atom through the β - PbO_2 layer.

3.3 Anodic durability of $\text{Ti/MO}_x/\beta$ - PbO_2 grids

In the following experiments, four oxides having rutile related structures, such as RuO_2 , IrO_2 , PtO_x and SnO_2 , were chosen as the MO_x layer and the anodic durability of the $\text{Ti/MO}_x/\beta$ - PbO_2 grids was examined, inferring that the best adhesion of oxide-oxide interfaces would be achieved by using the oxides having the similar crystal structure and volume of unit cell to each other. The anodic durability and potential of various $\text{Ti/MO}_x/\beta$ - PbO_2 grids examined at 100 mA/cm^2 are summarized in Table 1. It is clear that the anodic durability of

Table 1 Anodic durability and potential of Ti (mp)/ MO_x/β - PbO_2 grids

Grid	Anodic durability (h)	Potential (V vs. $\text{Hg/Hg}_2\text{SO}_4$)
$\text{Ti/SnO}_2(10^{-7})$ - $\text{SbO}_x(1.5 \times 10^{-8})/\beta$ - PbO_2	10	2.00
$\text{Ti/SnO}_2(10^{-6})$ - $\text{SbO}_x(1.5 \times 10^{-8})/\beta$ - PbO_2	19	1.87
$\text{Ti/PtO}_x(10^{-7})/\beta$ - PbO_2	13	1.90
$\text{Ti/IrO}_2(10^{-7})/\beta$ - PbO_2	18	1.70
$\text{Ti/RuO}_2(10^{-7})/\beta$ - PbO_2	19	1.78

grids with MO_x loadings of 10^{-7} mol of metal/ cm^2 increased in the order of SnO_2 , IrO_2 and RuO_2 . Although the Ti/PtO_x grid had very long anodic durability as described in the former section, the $\text{Ti/PtO}_x/\beta$ - PbO_2 grid had rather short anodic durability. This is probably due to the weak adhesion between PtO_x and β - PbO_2 , compared with the case of IrO_2 and

RuO_2 , resulting from the fact that the PtO_x is mainly composed of metallic Pt as described before. On the other hand, the Ti/SnO_2 - SbO_x/β - PbO_2 grid was expected to have the longest anodic durability among these four grids because SnO_2 has the volume of unit cell closest to that of β - PbO_2 , as can be seen from Table 2 in which some crystal data for MO_2 compounds having rutile-related structures, extracted from ref. 8), are given. Furthermore, Laitinen and Watkins¹⁹ have studied the mech-

Table 2 Crystal data for MO_2 Compounds having rutile related structures, extracted from ref. 8)

Oxide	a	b	c	V
TiO_2	4.594	—	2.958	62.43
RuO_2	4.4906 ± 2	—	3.1064 ± 2	62.64
IrO_2	4.4990 ± 2	—	3.1546 ± 2	63.85
β - PtO_2	4.4867 ± 4	4.5366 ± 4	3.1375 ± 5	63.85
SnO_2	4.738	—	3.188	71.57
β - PbO_2	4.955 ± 1	—	3.383 ± 2	83.06

anism of anodic deposition and cathodic stripping of PbO_2 on Sb-doped SnO_2 and concluded that the first fractional monolayer of PbO_2 was bonded directly to SnO_2 and was different from bulk PtO_2 . In Table 1, the anodic durability of $\text{Ti/SnO}_2(10^{-7})$ - $\text{SbO}_x(1.5 \times 10^{-8})/\beta$ - PbO_2 grid is relatively short. This is attributable to the ohmic resistance at the Ti/SnO_2 interface. However, the $\text{Ti/SnO}_2(10^{-6})$ - $\text{SbO}_x(1.5 \times 10^{-8})/\beta$ - PbO_2 grid revealed the long anodic durability comparable to the $\text{Ti/RuO}_2/\beta$ - PbO_2 grid. In order to reduce the ohmic resistance of Sb-doped SnO_2 bulk layer, some oxides with metallic conductivity, such as PtO_x , IrO_2 and RuO_2 , were added in the Sb-doped SnO_2 layer. The Ti/SnO_2 - SbO_x - MO_x/β - PbO_2 grids were examined at 100 mA/cm^2 . The anodic durability of grids increased in the order of SnO_2 - PtO_x , SnO_2 - IrO_2 and SnO_2 - RuO_2 . The experimental anodic durability and potential are summarized in Table 3. The anodic durability of the Ti/SnO_2 - SbO_x/β - PbO_2 grid was greatly extended by coexistence of RuO_2 or IrO_2 in the Sb-doped SnO_2 layer. Furthermore, it should be noted that the relative values for these grids corresponded to those for the $\text{Ti/MO}_x/\beta$ - PbO_2 grids except for the PtO_x containing grids. In the

Table 3 Anodic durability and potential of Ti (mp)/SnO₂-SbO_x-MO_x/β-PbO₂ grids

Grid	Anodic durability (h)	Potential (V vs. Hg/Hg ₂ SO ₄)
Ti/SnO ₂ (10 ⁻⁷)-SbO _x (1.5 × 10 ⁻⁹)-PtO _x (10 ⁻⁷)/β-PbO ₂	28	1.90
Ti/SnO ₂ (10 ⁻⁷)-SbO _x (1.5 × 10 ⁻⁹)-IrO ₂ (10 ⁻⁷)/β-PbO ₂	80	1.77
Ti/SnO ₂ (10 ⁻⁷)-SbO _x (1.5 × 10 ⁻⁹)-RuO ₂ (10 ⁻⁷)/β-PbO ₂	84	1.75

case of the Ti/SnO₂-SbO_x-PtO_x/β-PbO₂ grid, an addition effect of PtO_x was not significant, and the anodic durability was approximately equal to the algebraic sum of the anodic durability of the Ti/SnO₂-SbO_x/β-PbO₂ and Ti/PtO_x/β-PbO₂ grids. This is probably due to the partial isolation of PtO_x from Sb-doped SnO₂.

The dependence of the anodic durability of the Ti (mp)/SnO₂-SbO_x-IrO₂(10⁻⁷)/β-PbO₂ grid on the amount of SnO₂ loadings was examined. For the comparison, the anodic durability of the Ti (mp)/RuO₂(10⁻⁵) electrode in brine electrolysis was also examined under the same conditions. Figure 3 shows the variation of potential with anodization time at 100 mA/cm².

Fig. 3 Variation of potential with anodization time

- a) Ti(mp)/SnO₂(10⁻⁷)-SbO_x(1.5 × 10⁻⁹)-IrO₂(10⁻⁷)/β-PbO₂
- b) Ti(mp)/SnO₂(10⁻⁶)-SbO_x(1.5 × 10⁻⁸)-IrO₂(10⁻⁷)/β-PbO₂
- c) Ti(mp)/SnO₂(10⁻⁵)-SbO_x(1.5 × 10⁻⁷)-IrO₂(10⁻⁷)/β-PbO₂
- d) Ti(mp)/SnO₂(10⁻⁶)-SbO_x(1.5 × 10⁻⁸)-IrO₂(10⁻⁷)
- e) Ti(mp)/RuO₂(10⁻⁵)

The anodic durability of the Ti/SnO₂-SbO_x-IrO₂/β-PbO₂ grid increased with increasing amount of SnO₂ loadings but the potential was the lowest at 10⁻⁶mol of metal/cm². The anodic durability of the Ti(mp)/SnO₂(10⁻⁵)-SbO_x(1.5 × 10⁻⁷)-IrO₂(10⁻⁷)/β-PbO₂ grid was 2 times that of the Ti(mp)/RuO₂(10⁻⁵) electrode and was about 20 times that of the Ti(mp)/RuO₂(10⁻⁷)/β-PbO₂ grid²⁾. The anodic durability of this grid can be further increased by the surface treatment of titanium base and the service life of the Ti(ce)/SnO₂-SbO_x-IrO₂ or RuO₂/β-PbO₂/paste plate seems to be some thousand cycles, according to the speculation from the relationship of the DSA-type plate and grid³⁾. It was therefore considered that the Ti(ce)/SnO₂-SbO_x-IrO₂ or RuO₂/β-PbO₂ grid as a positive grid in lead-acid batteries had the sufficient anodic durability for the practical use.

In order to prove the reason for very long anodic durability of the Ti/SnO₂-SbO_x-IrO₂/β-PbO₂ grid, the surface and cross section morphologies of the Ti/SnO₂-SbO_x-IrO₂ and Ti/RuO₂ grids were examined by means of a scanning electron microscope (SEM). Microphotographs taken by SEM of the surface of these grids are shown in Fig. 4. The surface of the SnO₂-SbO_x-IrO₂ was very smooth, whereas the surface of the RuO₂ had large cracks. As can

Ti/SnO₂-SbO_x-IrO₂

Ti/RuO₂

Fig. 4 Microphotographs taken by SEM of surface of Ti(mp)/SnO₂(10⁻⁵)-SbO_x(1.5 × 10⁻⁷)-IrO₂(10⁻⁷) and Ti(mp)/RuO₂(10⁻⁵) grids

Fig. 5 Microphotographs taken by SEM of cross section of Ti (mp)/ $\text{SnO}_2(10^{-5})$ - $\text{SbO}_x(1.5 \times 10^{-7})$ - $\text{IrO}_2(10^{-7})$ and Ti(mp)/ $\text{RuO}_2(10^{-5})$ grids

a) Ti base, b) Oxide layer, c) Epoxy resin

be seen from Fig. 5, the thickness of SnO_2 - SbO_x - IrO_2 and RuO_2 layers was $0.6 \sim 1 \mu\text{m}$ and $1.2 \sim 1.4 \mu\text{m}$, respectively. The SnO_2 - SbO_x - IrO_2 layer was considered to be made up of very dense layer by increasing the density and the contraction of crystal lattice, as have been reported by Matsushita and Yamai¹⁰⁾. Such smooth surface and dense layer are fairly effective for retarding the passivation of the titanium base.

From the above results, it was clarified that the Sb-doped SnO_2 layer is very adhesive to both the titanium base and β - PbO_2 layer and that the addition of the oxides having the rutile-type structure and metallic conductivity, such as IrO_2 and RuO_2 , in the Sb-doped SnO_2 layer is very effective for increasing the anodic durability of Ti/SnO_2 - SbO_x/β - PbO_2 grid. In conclusion, it was proved that the Ti/SnO_x - SbO_x - MO_x/β - PbO_2 grids have a bright prospect of developing the new field of application as a positive grid in lead-acid batteries.

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References :

- 1) C. Iwakura, M. Inai and H. Tamura, *Chem. Lett.* (1977), 1407.
- 2) M. Inai, C. Iwakura and H. Tamura, *J. Appl. Electrochem.* **8**, 515 (1978).
- 3) M. Inai, C. Iwakura and H. Tamura, *J. Appl. Electrochem.* in press.
- 4) I.E. Veselovskaya, E.K. Spasskaya, V.A. Sokolov, V.I. Tkachenko and L.M. Yakimenko, *Élektrokhi-miya* **10** 70 (1974).
- 5) F. Hine, M. Yasuda and T. Yoshida, *J. Electrochem. Soc.* **124**, 500 (1977).
- 6) K. Fukuda, C. Iwakura and H. Tamura, *Electrochim. Acta*, in press.
- 7) B.N. Kavanov, E.S. Weisberg, I.L. Romanova and E.V. Krivolapova, *Electrochim. Acta* **9**, 1197 (1964).
- 8) D.B. Rogers, R.D. Shannon, A.W. Sleight and J.L. Gillson, *Inorg. Chem.* **8** 841 (1969).
- 9) H.A. Laitinen and N.H. Watkins, *J. Electrochem. Soc.* **123**, 804 (1976).
- 10) T. Matsushita and I. Yamai, *Yogyo Kyokaishi* **80**, 305 (1972).