JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 745–751

The improvement of the characteristics of DSA-type positive grids in lead-acid batteries by surface treatment of the titanium base

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Received 1 December 1978

The effect of surface treatment of the titanium base on the characteristics of the DSA-type positive grids and plates was examined, using mechanically polished, sandblasted and chemically etched titanium. It was found that the anodic durability of the grids and the service life of the plates were greatly increased and the self-discharge rate of the DSA-type plates was significantly decreased by sandblasting and chemical etching of the titanium base.

1. Introduction

During the study of DSA-type electrodes, it has been found that the Ti/RuO_2 electrode has promising characteristics as a positive grid in lead–acid batteries [1]. Further detailed investigations [2] have revealed that the Ti/RuO_2/β-PbO_2 electrode could be used to some extent as a positive grid. However, with use over long times the Ti/RuO_2 and Ti/RuO_2/β-PbO_2 grids might have the following problems: (a) shedding of paste (active material) occurs because of the lack of adhesion of the paste to the grid, (b) lowering of the discharge efficiency and significant self-discharge of the plate occur because of the low oxygen overvoltage of the RuO_2 layer and (c) deterioration of the charge–discharge performance occurs because of the development of an additional ohmic resistance at the Ti/RuO_2 interface, i.e. the passivation of the titanium base. However, problems (a) and (c) should be solved by using a roughened titanium base in place of the smooth titanium sheet in order to produce good adhesion of the oxide layer to the base and the minimum electrical interface resistance.

In general, a sandblasted or etched titanium base is preferable as the DSA base material to which the coating solution is applied [3]. Fukuzuka *et al.* [4] have reported that the resistance of the PbO_2-coated titanium electrode due to the formation of an insulating film on the titanium base was changed by the following pre-treatments: vacuum annealing, pickling, polishing and sandblasting. They were performed in this order as it causes an increase in the surface roughness of the pre-treated titanium base which increases the interfacial adherence and decreases the particle gap of electrodeposited PbO_2. Higley *et al.* [5] have also claimed that sandblasting appeared to be best for obtaining good PbO_2 adherence to the titanium base. These authors [4, 5] seemed to consider that a PbO_2 adherence to the titanium base resulted only from mechanical bonding of the plated PbO_2 with the base. On the other hand, Wabner *et al.* [6] have proposed a novel process for the preparation of PbO_2-coated titanium anodes in which the most important step was a treatment of the clean surface with a Ti(IV)-containing solution, i.e. an adsorption of Ti(IV) oxalate at the titanium surface. Besides these treatments, Faber [7] has extensively surveyed the methods for titanium surface preparation, and he has shown that it is possible to use the PbO_2-coated titanium (Ti/PbO_2) for the positive grids of lead accumulators.

In this work, the effect of surface treatment of the titanium base on the characteristics of the

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DSA-type positive grids in lead–acid batteries was examined, using the mechanically polished, sandblasted and chemically etched titanium.

2. Experimental

The surface of the titanium base ($2{\cdot}54\ \mathrm{cm}^2$) was pre-treated by three different methods: mechanical polishing with emery paper (no. 1500), sandblasting with white alundum (no. 120) in an atmosphere of nitrogen for 6 s and chemical etching with boiling 15 wt% oxalic acid solution for 1 h. The chemical etching procedure is similar to that reported by Wabner *et al.* [6]. These pre-treated titanium bases will be referred to as Ti(mp), Ti(sb) and Ti(ce), respectively. The RuO_2 coating was achieved by thermal decomposition of $RuCl_3$ on such a titanium base. The amount of RuO_2 loadings ranged from 10^{-5}–$10^{-7}\ \mathrm{mol\ cm^{-2}}$ in this work. Sometimes, the β-PbO_2 layer ($5 \times 10^{-5}\ \mathrm{mol\ cm^{-2}}$) was further electrodeposited on the surface of the Ti/RuO_2 grid from the plating bath of 21% $Pb(NO_3)_2$ solution. The standard pasting procedure similar to that described in [8], using Pb and PbO mixed powders, was employed in the preparation of the positive plate. After pasting, the plates were formed in 1·050 sp. gr. H_2SO_4 prior to use in the charge–discharge tests. All electrochemical measurements were carried out in 1·290 sp. gr. H_2SO_4 at 25° C by the same methods as those described previously [2]. A platinum sheet and a mercury–mercurous sulphate electrode (Hg/Hg_2SO_4) were used as counter and reference electrodes, respectively. The detailed measuring conditions will be given separately in the next section.

3. Results and discussion

3.1. *Anodic characteristics of grids*

In a previous paper [2], it was shown that the optimum amount of RuO_2 loading on the Ti(mp) base was about $10^{-7}\ \mathrm{mol\ cm^{-2}}$ in order to charge the positive plate efficiently with minimum loss of current in the possible side reaction of oxygen evolution from the surface of the Ti(mp)/RuO_2 grid. Since the surfaces of Ti(sb) and Ti(ce) bases are very rough, compared with that of the Ti(mp) base, the RuO_2 loadings on the former titanium bases, on the latter base, corresponding to $10^{-7}\ \mathrm{mol\ cm^{-2}}$ were evaluated. For this purpose, the oxygen evolution current on the Ti(ce)/RuO_2 grid was measured by means of cyclic voltammetry using a sweep rate of $10\ \mathrm{mV\ s^{-1}}$ in the potential range of 0·75–1·65 V. Fig. 1 shows the plot of oxygen evolution current at 1·65 V against the amount of RuO_2 loading. As described in the previous paper [2], the oxygen evolution current increased linearly with an increase in the RuO_2 loading on the Ti(mp)/RuO_2 grid and the line had unit slope. On the Ti(ce)/RuO_2 grid, however, two linear parts appeared in the relationship between the oxygen evolution current and the RuO_2 loading: one having a unit slope ranged from 1×10^{-7}–$5 \times 10^{-7}\ \mathrm{mol\ cm^{-2}}$ and the other having a slope of 0·5 ranged from 5×10^{-7}–$10^{-5}\ \mathrm{mol\ cm^{-2}}$. The latter value of the slope indicates that about one half of the RuO_2 loading was ineffective for the oxygen evolution reaction. On the basis of these results, it is considered that the RuO_2 layer on the Ti(ce) base was closely packed in the small space or hole on the bumpy surface of the Ti(ce) base and one half of the RuO_2 layer was not exposed to the solution. Since the oxygen evolution current observed on the Ti(ce) grid with a RuO_2 loading of $2 \times 10^{-7}\ \mathrm{mol\ cm^{-2}}$ was almost the same as that on the Ti(mp) grid with a RuO_2 loading of $10^{-7}\ \mathrm{mol\ cm^{-2}}$, as can be seen from Fig. 1. A RuO_2 loading of $10^{-7}\ \mathrm{mol\ cm^{-2}}$ was employed for the Ti(ce)/RuO_2 grid, in the later experiments.

It was shown in a previous paper [2] that the service life of the DSA-type plates is determined by the anodic durability of the grids, resulting from the passivation of the titanium base. Hence, the anodic durabilities of the Ti(mp)/RuO_2/

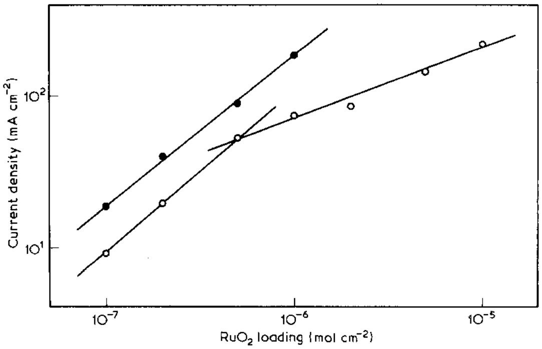

Fig. 1. Plot of oxygen evolution current at 1·65 V against RuO_2 loading. ●, Ti(mp)/RuO_2; ○, Ti(ce)/RuO_2.

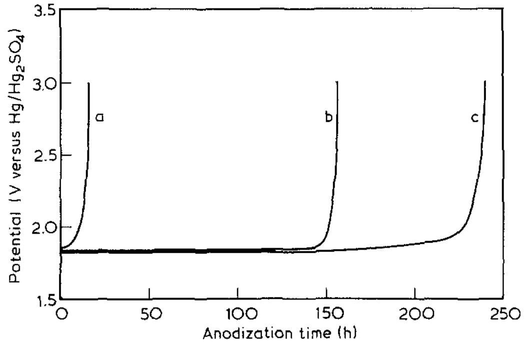

Fig. 2. Variation of potential with anodization time at 100 mA cm^{-2}. (a) Ti(mp)/RuO$_2$/β-PbO$_2$, (b) Ti(sb)/RuO$_2$/β-PbO$_2$, (c) Ti(ce)/RuO$_2$/β-PbO$_2$.

β-PbO$_2$, Ti(sb)/RuO$_2$/β-PbO$_2$ and Ti(ce)/RuO$_2$/β-PbO$_2$ grids were tested under galvanostatic conditions at 100 mA cm^{-2} in 1·290 sp. gr. H$_2$SO$_4$. Fig. 2 shows the variation of potential with anodization time for these grids. The anodic durability of the grid was defined as the anodization time until a potential of 3·0 V versus Hg/Hg$_2$SO$_4$ was reached. The data obtained, together with the relative values, are given in Table 1. The anodic durabilities of the Ti(mp)/RuO$_2$/β-PbO$_2$, Ti(sb)/RuO$_2$/β-PbO$_2$ and Ti(ce)/RuO$_2$/β-PbO$_2$ grids were 15 h, 156 h and 240 h, respectively. Evidently, the pretreatment of the titanium surface by sandblasting or chemical etching is highly effective for retarding the passivation of the titanium base.

In order to prove the reason for the long anodic durability of the DSA-type grids with the Ti(sb) and Ti(ce) bases, the surface and the cross-section morphologies of the grids were examined by a scanning electron microscope (Hitachi-Akashi MINI-SEM, MSM-7C). Microphotographs taken by SEM of the surface of titanium bases are shown in Fig. 3. The surface of the Ti(mp) base was smooth whereas the surfaces of the Ti(sb) and Ti(ce) bases were bumpy. Particularly in the case of the Ti(ce) base, many projections of several μm height were observed on the surface. Such bumpy surfaces of the pre-treated bases were considered to be active chemically and physically, and then effective for the adhesion of RuO$_2$ and β-PbO$_2$ layers. The microphotographs of the cross-sections of Ti(mp)/RuO$_2$/β-PbO$_2$ and Ti(ce)/RuO$_2$/β-PbO$_2$ grids are shown in Fig. 4. Evidently the interface between Ti(mp)/RuO$_2$ and β-PbO$_2$ is very smooth, whereas the interface between Ti(ce)/RuO$_2$ and β-PbO$_2$ is very rough. The RuO$_2$ layer was so thin that it could not be observed clearly. In the case of the latter grid, the electrodeposited β-PbO$_2$ layer adheres closely to the Ti/RuO$_2$ base and is densely packed even in the small space of the projection on the Ti(ce)/RuO$_2$ surface. Such a β-PbO$_2$ layer seems to result in an increase of its adhesion to the substrate and hence the durability of the grid.

Table 1. Effect of surface treatment of titanium base on anodic durability of grid

Grid	*Anodic durability* (h)	*Relative value*
Ti(mp)/RuO$_2$/β-PbO$_2$	15	1
Ti(sb)/RuO$_2$/β-PbO$_2$	156	10
Ti(ce)/RuO$_2$/β-PbO$_2$	240	16

3.2. *Charge–discharge characteristics of plates*

The charge–discharge characteristics of the plates in 1·290 sp.gr. H$_2$SO$_4$ were measured under galvanostatic conditions: the plates were charged at 12 mA cm^{-2} for 105 min and then discharged at 64 mA cm^{-2} for 15 min, and this operation was repeated many times. In this measurement, one of the two time-switches with different precisions (TU-16H and TU-6H, Mitsubishi Electric Corp. Ltd) was used for the control of charge–discharge time. One time-switch (TU-16H) controlled the time with an error of ± 0·7 min/15 min and the other time-switch (TU-6H) with an error of ± 4·5 min/15 min. The service life of the plate was defined as the number of cycles before the potential at the end of discharge was reached, 0·75 V versus Hg/Hg$_2$SO$_4$. In order to retard the shedding of the paste, a plastic sheet with micropores (Yumicron, supplied from Yuasa Battery Co. Ltd) was placed on the positive plate prior to the forming of the plate. The variation of potential with cycling is shown in Fig. 5. The solid and dotted lines show the data obtained by using the time-switches TU-16H and TU-6H, respectively. The significant difference in the appearance at the end of service life was observed between the Pb and DSA-type plates. In the case of the Pb plate, the end of service life appeared suddenly whereas it was less defined with the DSA-type plate. Furthermore, it is clear that the service life of the Ti(ce)/

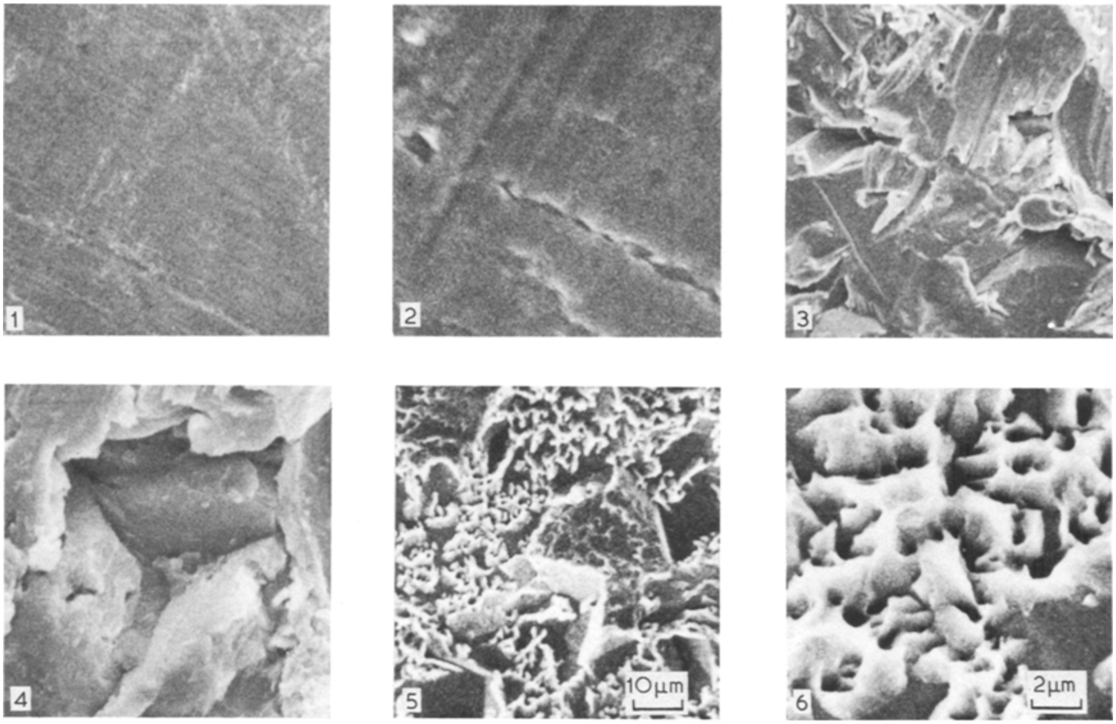

Fig. 3. SEM micrographs of titanium surfaces. 1, 2 Ti(mp); 3, 4, Ti(sb); 5, 6, Ti(ce). 1, 3 and 5, × 650; 2, 4 and 6, × 3200.

RuO_2/β-PbO_2/paste plate was about twice that of the Pb/paste plate. Some of the service lives of plates are given in Table 2. The relative values are also given in the last column of this table. As can be seen from the relative values, the service lives of the DSA-type plates were almost proportional to the anodic durability of the DSA-type grid given in Table 1.

From these results, it was confirmed that the limitation of the service life of the DSA-type plate was mainly caused by the passivation of the titanium base and the service life of the DSA-type plate can be estimated from the anodic durability of the grid. The relationship between the anodic durability of grid and service life of the plate is summarized in Table 3. The service life of the Ti(ce)/RuO_2/β-PbO_2/paste plate deviates from the linear relationship between the anodic durability

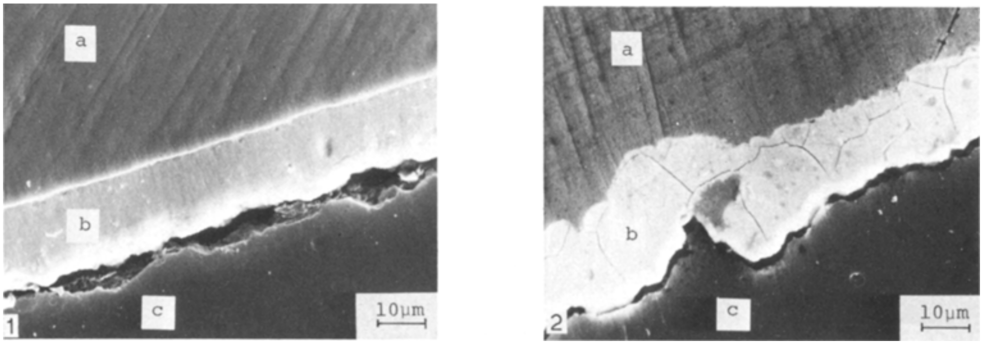

Fig. 4. SEM micrographs of Ti/RuO_2/β-PbO_2 grid cross-sections. (a) Ti base; (b) β-PbO_2 layer, (c) epoxy resin. (× 650).

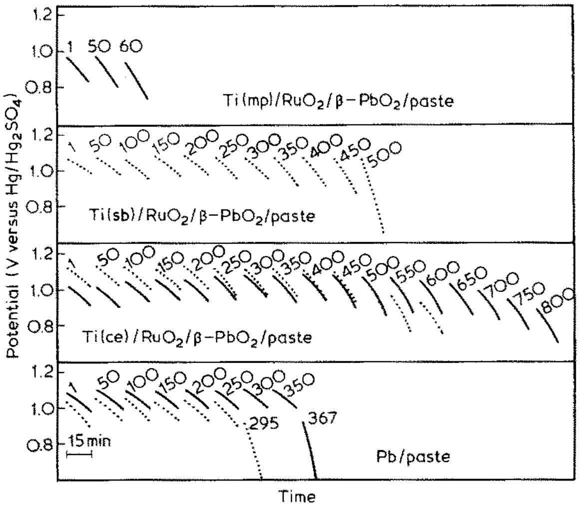

Fig. 5. Variation of potential with charge/discharge cycle number. The solid and dotted lines show data obtained by using time-switches TU-16H and TU-6H, respectively.

of grids and the service life of plates, and this may be partly determined by the deterioration of the paste. The results obtained in this study may or may not be directly compared with published data for the standard battery plates, but, in the paste-type battery the positive plates using the Pb–Sb alloy grid typically have a service life of 100–400 cycles [8] because of the low valency Pb oxide layer formed by the grid corrosion and the deterioration of the paste bulk. In the DSA-type plates, however, such grid corrosion does not occur and hence the DSA-type grids have a long service life and low self-discharge rate compared with Pb and Pb–Sb alloy grids.

3.3. *Self-discharge characteristics of plates*

In the usual Pb/paste positive plates, the self-discharge occurs by two important processes: the local cell reaction between β-PbO$_2$ and electrolyte

$$\beta\text{-PbO}_2 + H_2SO_4 \rightarrow PbSO_4 + H_2O + 1/2O_2$$

and the reaction between β-PbO$_2$ and the metallic Pb grid [9]

$$\beta\text{-PbO}_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O.$$

In the case of DSA-type plates, however, the latter process is ruled out and the following local cell reaction proceeds. The anodic partial reaction is oxygen evolution from water

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

and the cathodic partial reaction is formation of PbSO$_4$ from β-PbO$_2$

$$\beta\text{-PbO}_2 + H_2SO_4 + 2H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O,$$

As reported in the previous paper [2], the relative self-discharge rate of DSA-type positive plates can be estimated from the current at an intersecting point of the anodic polarization curves of the grids with the cathodic polarization curve of the Pb/paste plate. Fig. 6 shows the anodic polarization curves of the DSA-type grids and the cathodic

Table 2. Effect of surface treatment of titanium base on service life of plate

Plate	*Service life* (times)	*Relative value*
Ti(mp)/RuO$_2$/β-PbO$_2$/paste	60*	1*
Ti(sb)/RuO$_2$/β-PbO$_2$/paste	480†	10†
Ti(ce)/RuO$_2$/β-PbO$_2$/paste	770*, 600†	13*, 13†
Pb/paste	367*, 295†	6*, 6†

* Data obtained using time-switch TU-16H.
† Data obtained using time-switch TU-6H.

Table 3. Relationship between anodic durability of grid and service life of plate

Titanium base	*Anodic durability of grid*	*Service life of plate*
Ti(mp)	1	× 4
Ti(sb)	10	× 40
Ti(ce)	16	× 52

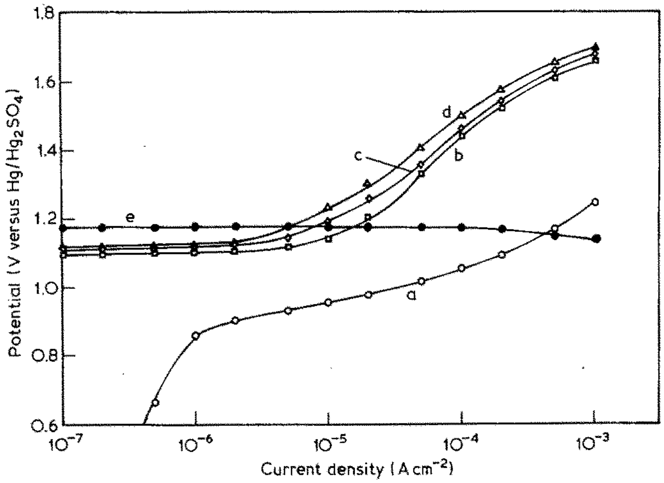

Fig. 6. Galvanostatic polarization curves of DSA-type grids and Pb/paste plate. (a) Ti(mp)/RuO$_2$, (b) Ti(mp)/RuO$_2$/β-PbO$_2$, (c) Ti(sb)/RuO$_2$/β-PbO$_2$, (d) Ti(ce)/RuO$_2$/β-PbO$_2$, (e) Pb/paste.

polarization curve of the Pb/paste plate. Since the β-PbO$_2$ layer was densely electrodeposited on the bumpy surface of the Ti(sb)/RuO$_2$ and Ti(ce)/RuO$_2$ substrates, the influence of the presence of the RuO$_2$ layer on the lowering of the potential was small and the anodic polarization curves of these grids were to more anodic potentials, compared with the Ti(mp)/RuO$_2$/β-PbO$_2$ grid. The currents at the intersecting points of the partial polarization curves and the self-discharge rate are summarized in Table 4. The values of the self-discharge rate for the Ti(sb)/RuO$_2$/β-PbO$_2$/paste and Ti(ce)/RuO$_2$/β-PbO$_2$/paste plates were estimated from the current at an intersecting point of the partial polarization curves while the values for the other plates were experimentally measured in the previous work [2]. It is evident that the self-discharge rate of the DSA-type plates is significantly decreased by sandblasting or chemical etching of the titanium base. For example, the self-discharge rate of the Ti(ce)/RuO$_2$/β-PbO$_2$/paste plate was estimated to be about one-fifth of that of the Pb/paste plate.

4. Summary

The effect of surface treatment of the titanium base on the characteristics of the DSA-type positive grids and plates were examined in 1·290 sp. gr. H$_2$SO$_4$, and the main conclusions to be drawn from the results are as follows:

(a) The anodic durability of the DSA-type grids and the service life of the DSA-type plates were greatly increased by sandblasting and chemical etching of the titanium base: e.g. the service life of the Ti(ce)/RuO$_2$/β-PbO$_2$/paste plate was twice that of the Pb/paste plate.

(b) The service life of the DSA-type plate can be estimated from the anodic durability of the grid, so long as the passivation of the titanium base determines the plate's life.

(c) The self-discharge rate of the DSA-type plates was significantly decreased by sandblasting and chemical etching of the titanium base: e.g. the self-discharge rate of the Ti(ce)/RuO$_2$/β-PbO$_2$/paste plate was estimated to be about one-fifth that of the Pb/paste plate.

Table 4. Self-discharge rates of plates

Plate	*Current at a point of intersection* (A cm^{-2})	*Self-discharge rate* (%/day)	*Relative value*
Ti(mp)/RuO$_2$/paste	4×10^{-4}	5·4	27
Ti(mp)/RuO$_2$/β-PbO$_2$/paste	$1·5 \times 10^{-5}$	0·2	1
Ti(sb)/RuO$_2$/β-PbO$_2$/paste	8×10^{-6}	0·11 (estimated)	0·53
Ti(ce)/RuO$_2$/β-PbO$_2$/paste	5×10^{-6}	0·07 (estimated)	0·33
Pb/paste		0·3	1·5

Acknowledgement

The authors express their appreciation to Yuasa Battery Co. Ltd for providing the necessary facilities.

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