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AUTHOR(S):

NISHIHARA, Kiyokado; KURACHI, Mitsuo; HAYASHI, Minoru; HASHIMOTO, Tamotsu

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# Internal Stress in Electrodeposited $\text{PbO}_2$

by

Kiyokado NISHIHARA, Mitsuo KURACHI, Minoru HAYASHI  
and Tamotsu HASHIMOTO

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The change of internal stress in the electrodeposited  $\text{PbO}_2$  from a lead nitrate bath was observed by measuring the deflection of a thin platinum anode during electrodeposition of  $\text{PbO}_2$  on one side of it. The crystal structure of the deposits was determined by X-ray diffraction. After the electrodeposition, the change of deflection of the deposited  $\text{PbO}_2$  was observed under the following conditions:

- a) Keep the deposited  $\text{PbO}_2$  in air or in a lead nitrate bath at constant temperatures.
- b) Discharge the cell,  $\text{Pt/PbNO}_3$  electrolyte/ $\text{PbO}_2$  deposit, by connecting it to an external circuit with some resistance.

The results obtained are summarized as follows:

- 1) The crystal structure of  $\alpha$ - $\text{PbO}_2$  was observed in the deposits which had deflected in the direction of contraction during electrodeposition, and  $\beta$ - $\text{PbO}_2$  was observed in the deposits which had deflected in the direction of expansion during electrodeposition.
- 2) After the electrodeposition, the deposits deflected gradually in the direction of expansion when they were kept in air or left in the bath. The amount of deflection of the deposits of  $\alpha$ - $\text{PbO}_2$  was larger than that of the deposits of  $\beta$ - $\text{PbO}_2$  within the same time duration.
- 3) The electrodeposited  $\text{PbO}_2$  deflected in the direction of expansion by discharging the cell, and the amount of deflection of the deposits of  $\alpha$ - $\text{PbO}_2$  was larger than that of the deposits of  $\beta$ - $\text{PbO}_2$ .

## 1. Introduction

Electrodeposited  $\text{PbO}_2$  is useful for the anode of electrolytic production of perchlorate and persulphate. Also  $\text{PbO}_2$  is produced at the anode when a lead storage battery is charged, this  $\text{PbO}_2$  works as the active material for the cell.

In the previous works by Shibasaki<sup>1)-2)</sup> and Koizumi<sup>3)</sup>, two different properties have been observed depending on the electrolysis conditions: one is deflection in the direction of contraction, and the other is deflection in the direction of expansion during electrolysis. Also with regard to a crystal structure of  $\text{PbO}_2$ , it has been

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Department of Metallurgy, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto, Japan.

found that two diverse types,  $\alpha$ - $\text{PbO}_2$  (tetragonal) and  $\beta$ - $\text{PbO}_2$  (orthorhombic) exist<sup>(6)-8)</sup>. If the deflection ever exists in electrodeposited  $\text{PbO}_2$ , it might cause deformation or decay of the anode when  $\text{PbO}_2$  is used as the anode material. Therefore, it is an urgent problem of technique to explore the true reason of the deflection and to find the condition which enable us to remove such deflection. But with regard to the relation between deflection and crystal structure and also to the change of deflection in  $\text{PbO}_2$  during the discharge or the charge of a lead storage battery, there remain a number of fundamental problems yet to be solved.

We shall in this paper investigate the relation between the change of deflection and the change of crystal structure of electrodeposited  $\text{PbO}_2$ , and thus try to obtain further perspective on the change of deflection in electrodeposited  $\text{PbO}_2$ . The observations were made during electrodeposition of  $\text{PbO}_2$  from a lead nitrate electrolytic bath, after electrodeposition, and also during the discharge process.

## 2. Apparatus and Experimental Methods

The chemical grade reagents were used for preparing the electrolytic bath containing 1 mol/l lead nitrate and 0.1 mol/l copper nitrate. The hydrogen ion concentration in the bath was maintained 2 by pH unit by using basic lead carbonate

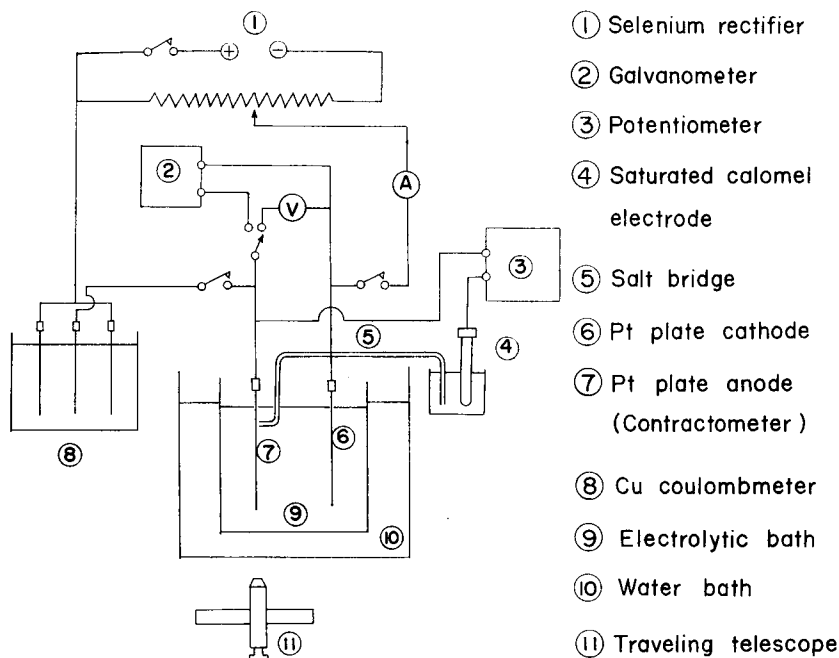


Fig. 1. Schematic diagram of electrolytic apparatus.

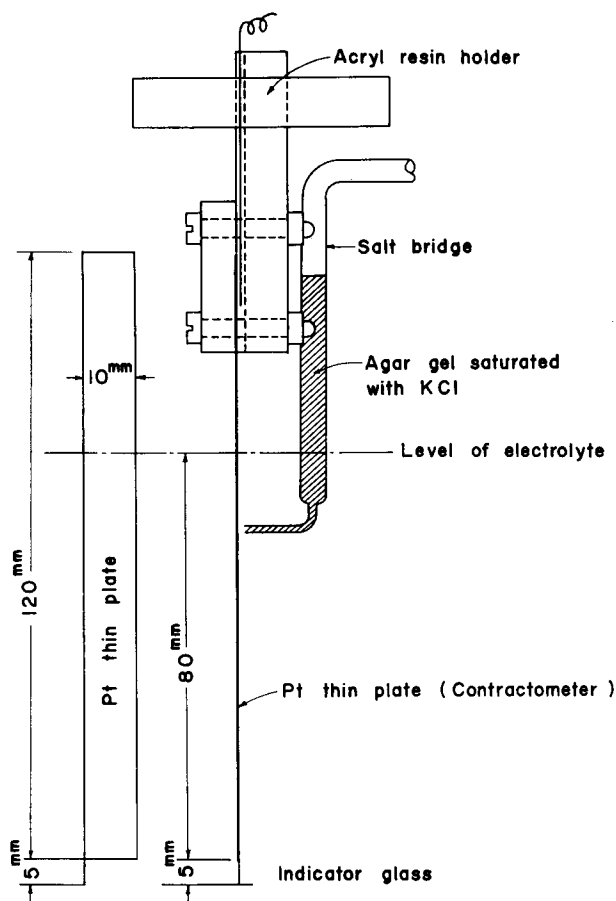


Fig. 2. Platinum thin plate contractometer.

or nitric acid. Fig. 1 shows the schematic diagram of the electrolytic apparatus.

The bending of a thin platinum plate, namely a contractometer, due to the deposition of  $PbO_2$  on one side of it, was referred to as the internal stress in the deposited  $PbO_2$ . The platinum plate used as a contractometer was 100 mm in length, 10 mm in width and 0.3 mm in thickness, as shown in Fig. 2. The effective anode surface for the electrodeposition of  $PbO_2$  was 80 mm in length and 10 mm in width. The cathode platinum plate had the same dimension of the anode. They were fixed at given positions in the electrolytic cell by the support of acryl resin holder respectively. The bending was measured by the deflection of a needle at the free-end of contractometer. The deflection caused by the deposits was observed by travelling telescope during the electrodeposition and then again when the plate was exposed in air or in the bath. Subsequently, the measurements were continued

Table 1 Measuring condition of X-ray diffraction

Target	:	Cu
Filter	:	Ni
Tube voltage	:	35 kV
Tube current	:	15 mA
Slit width	:	4-0.2 mm
Time constant	:	5 sec
Full scale	:	200 or 500 c.p.s.
Scanning speed	:	1°/min
Chart speed	:	10 mm/min
High tension voltage	:	1,500 V

during the discharge of the cell, Pt/PbNO<sub>3</sub> electrolyte/PbO<sub>2</sub> by connecting to an external circuit with some resistance. The strength of discharging currents was measured and recorded by means of galvano-recorder which was produced by Yanagimoto Co., Ltd. The change in the potential of PbO<sub>2</sub> electrode during discharge was measured by vacuum tube potentiometer. A saturated calomel electrode was used as the reference electrode.

The X-ray diffractions of the deposits were measured under the conditions shown in Table 1. The identification of crystal structure was made by comparing X-ray diffraction patterns with A.S.T.M. cards and also with standard sample of PbO<sub>2</sub> made by MERK company. The X-ray automatic recording diffraction apparatus GX-4 B produced by Shimazu manufacturing Co. was used.

### 3. Change of Deflection and Potential during Electrodeposition

Shibasaki et al.<sup>12-33</sup> have reported that the deflection takes place in two ways, one towards the direction of expansion and other towards the direction of contraction, depending on the conditions of electrolysis, such as temperature and current density et al.

In this paper, the electrolysis carried out under the following conditions: Bath composition, 1.0 mol/l PbNO<sub>3</sub>, and pH unit 2; Bath temperature, 10°C or 30°C; Anode current density, 1 A/dm<sup>2</sup> or 3 A/dm<sup>2</sup>; Duration time of electrodeposition, 24 min.

The change of deflection and the change of electrode potential of the deposit were observed during the electrodeposition of PbO<sub>2</sub>. The results obtained are shown in Fig. 3. In the early stage of electrodeposition, the direction of deflection went towards the contraction in all case, after a while the direction of deflection was changes by the electrolytic conditions.

When the electrodeposition was carried out at a temperature of 30°C and an

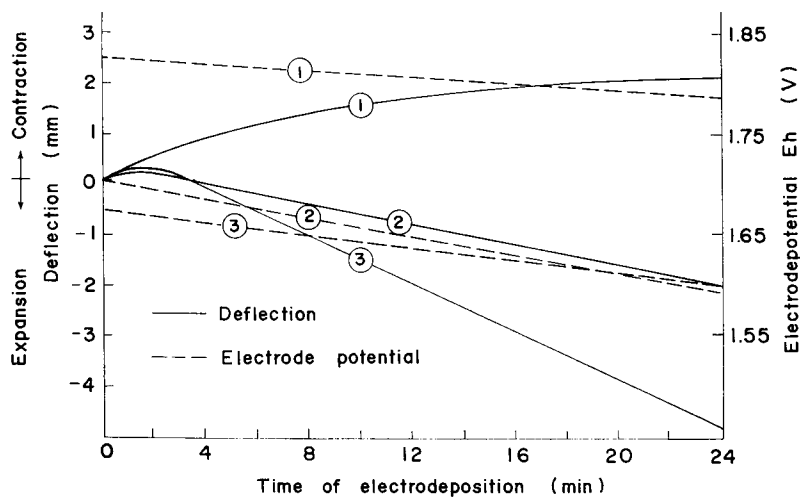


Fig. 3. The change of deflection and electrode potential of the deposits during electrodeposition.

①  $10^\circ\text{C}$ ,  $3 \text{ A/dm}^2$ ; ②  $10^\circ\text{C}$ ,  $1 \text{ A/dm}^2$ ; ③  $30^\circ\text{C}$ ,  $3 \text{ A/dm}^2$

anode current density of  $3 \text{ A/dm}^2$  or at  $10^\circ\text{C}$  and  $1 \text{ A/dm}^2$ , the deflection went eventually towards the direction of expansion, while when the electrodeposition carried out at  $10^\circ\text{C}$  and  $3 \text{ A/dm}^2$ , the deflection went again in the direction of contraction. In any condition for electrolysis, the current efficiency for the electrodeposition was always about 100 percent, and the quantities deposited for the equal magnitudes of currents were approximately the same.

As shown by the dotted lines in Fig. 3, the potential of  $\text{PbO}_2$  during the electrodeposition is high in the early stage of deposition, but in the course of time of electrolysis it linearly declined. Further more it was noticed that, the lower the bath temperature and the higher the current density the potential became higher.

With regard to the surface condition of electrodeposit, it was found that  $\text{PbO}_2$  which deflected towards contraction had smooth and fine luster, but  $\text{PbO}_2$  which deflected towards expansion showed less luster.

With regard to the X-ray diffraction lines on the surface of  $\text{PbO}_2$  (access to the Pt plate) which, at the early stage of electrolysis, deflected in the direction of contraction, three strong diffraction lines were observed. These lines correspond to the (020) plane of  $\alpha\text{-PbO}_2$ , the (301) plane and the (213) plane of  $\beta\text{-PbO}_2$ , respectively. Among them the line corresponding to the plane of  $\alpha\text{-PbO}_2$  was the strongest.

Among the X-ray diffraction lines on the electrodeposition surface of  $\text{PbO}_2$  which deflected to the direction of contraction even until the end of electrolysis, the diffraction lines of the (020) plane of  $\alpha\text{-PbO}_2$  were prominent and showed the largest intensity ratio, and the accompanied several diffraction lines of  $\beta\text{-PbO}_2$  and

of other crystal structure of  $\text{PbO}_2$  were of small intensity ratio.

Among the X-ray diffraction lines of  $\text{PbO}_2$  on the electrodeposition which deflected towards the direction of expansion at the end of electrolysis, the line corresponding to the (101) plane of  $\beta\text{-PbO}_2$  were prominent and showed the largest intensity ratio, and the diffraction lines corresponding to the (020) plane of  $\alpha\text{-PbO}_2$  were of smaller intensity ratio.

#### 4. Change of Deflection when the Electrodeposited $\text{PbO}_2$ is kept in Air

Fig. 4 shows the deflection of  $\text{PbO}_2$  deposited under the same condition of electrolysis described in the previous section. In this case, the amount of deposits was  $20 \text{ A}\cdot\text{min}/\text{dm}^2$ . During electrodeposition, the contractile deflection of  $\text{PbO}_2$  deposited from the bath at  $10^\circ\text{C}$  and  $3 \text{ A}/\text{dm}^2$  was observed, and the expansive deflection of  $\text{PbO}_2$  deposited from the bath at  $30^\circ\text{C}$  and  $3 \text{ A}/\text{dm}^2$  was larger than that of  $\text{PbO}_2$  deposited from the bath at  $10^\circ\text{C}$  and  $1 \text{ A}/\text{dm}^2$ . On being exposed in air, the contractile deflection of  $\text{PbO}_2$  decreased markedly and tended to the expansive deflection, and the expansive deflection of  $\text{PbO}_2$  increased slightly. The extent of the change of deflection towards the direction of expansion was found to be larger for the case of  $\alpha\text{-PbO}_2$  which, during electrolysis, deflected towards the direction of contraction than for the case of  $\beta\text{-PbO}_2$  which deflected towards the direction of expansion during electrolysis.

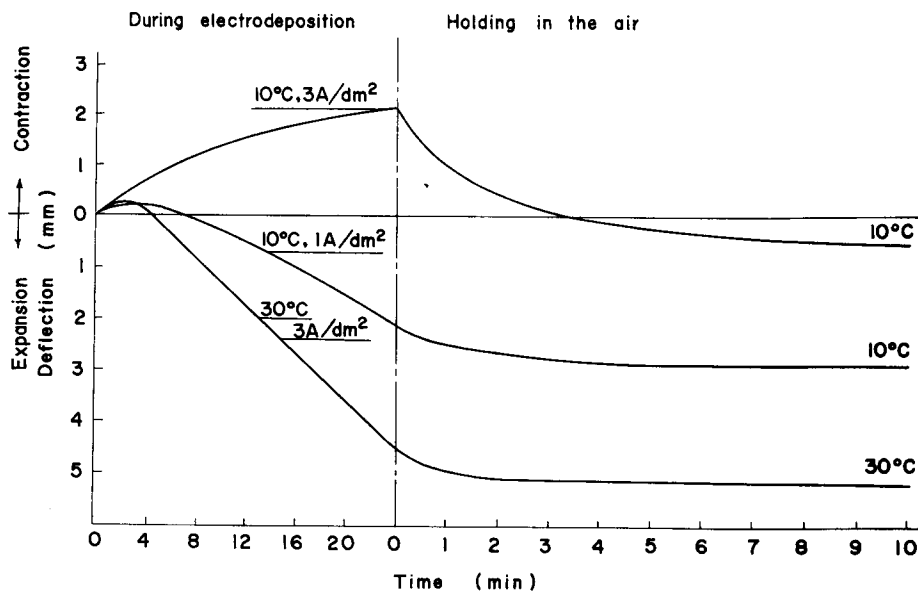


Fig. 4. The change of deflection of the deposit during electrodeposition and holding it in air.

### 5. Change of Deflection when the Electrodeposited $PbO_2$ is discharged in the $PbNO_3$ Electrolytic Bath

The electrodeposited  $PbO_2$  which deflected either in the direction of expansion or in the direction of contraction during electrolysis was kept in the electrolytic bath as it was after electrolysis and used as the anode of the cell, Pt/ $PbNO_3$  electrolyte/ $PbO_2$ , connected with resistors of various capacity in series and discharged.

Thus, the relation between the discharge current density and the change of deflection was observed.

#### 5.1 Discharge of $PbO_2$ deflected towards the direction of contraction during electrodeposition

The  $PbO_2$  deflected towards the direction of contraction during electrodeposition was obtained from the bath at  $10^\circ C$  and  $3 A/dm^2$ . The change of deflection and the current density was observed at  $10^\circ C$ .

As shown in Fig. 5, during discharge the change of deflection is observed toward the direction of expansion. The rate of change of deflection decreased, as the resistance in the circuit increased. When a resistor with 10 k ohms was used, the change of deflection was reduced approximately equal to that of deflection which was observed in the case where  $PbO_2$  alone was held in the bath by opening the circuit.

As shown in Fig. 6 the change of current density was observed to decrease linearly in time of discharge for all cases. It also was found that the current density

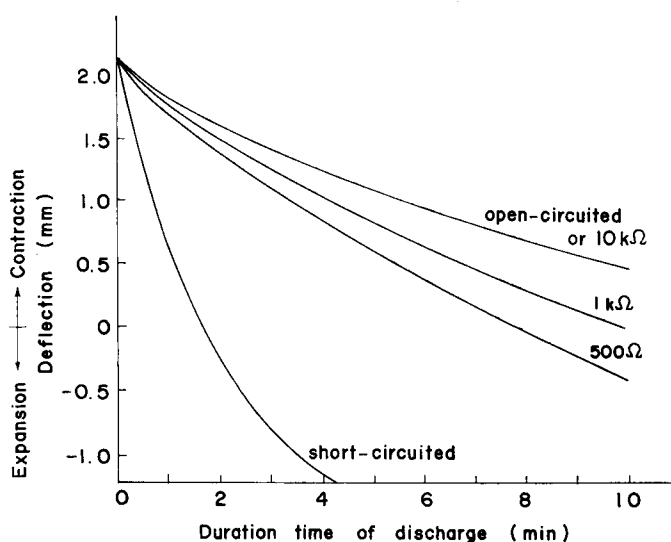


Fig. 5. The change of deflection of the deposits during discharge. (at  $10^\circ C$ ).



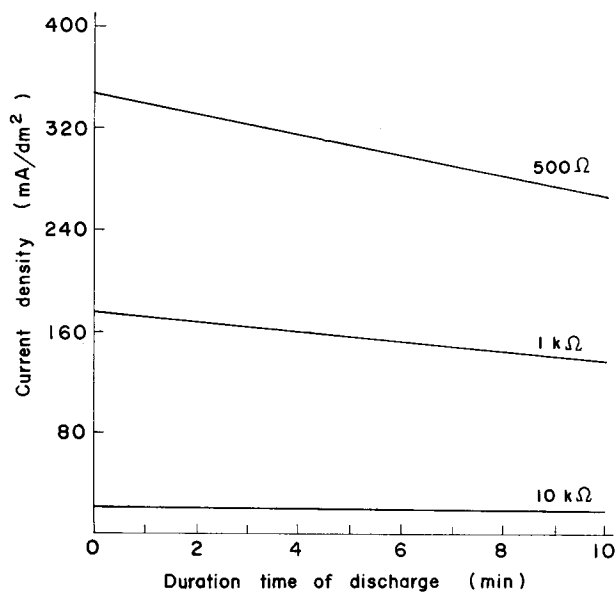


Fig. 6. The change of current density during discharge. (at 10°C).

at the early stage of discharge was higher as the resistance of the circuit is smaller, and that the rate of decrease in time of that current density for discharge became larger as the resistance of discharging circuit is smaller.

5.2. Discharge of PbO<sub>2</sub> deflected to the direction of expansion during electro-deposition

The PbO<sub>2</sub> deflected towards the direction of expansion during electrodeposition

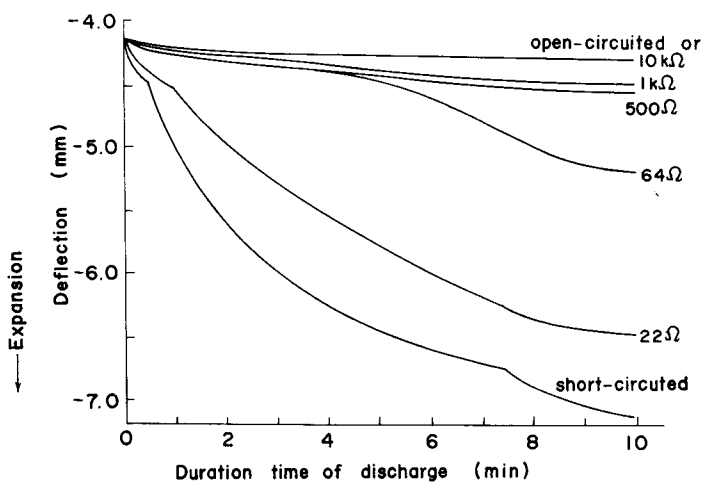


Fig. 7. The change of deflection of the deposit during discharge in the bath at 30°C.

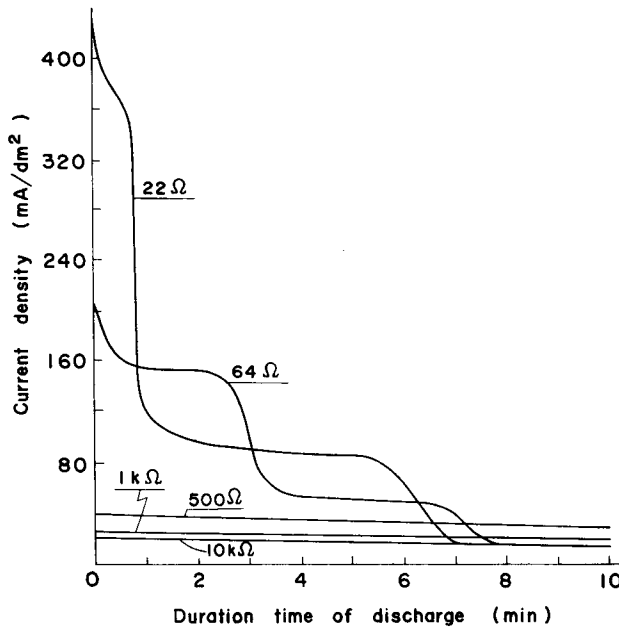


Fig. 8. The change of current density during discharge in the bath at 30°C.

was obtained from the bath at 30°C and 3 A/dm<sup>2</sup>. The change of deflection and of current density were measured at 30°C. As shown in Fig. 7 during discharge the change of deflection was observed in the direction of expansion in the course of time duration. When the discharge circuit was short-circuited, the change of deflection became maximum, and when the resistance of the circuit was small, the deflection varied stepwise and rapidly. The change of deflection when the resistor with 10 k ohms was inserted was found to reduce to the change of deflection that was observed in the case when the  $PbO_2$  was alone left in the bath by the opening circuit.

From Fig. 8, the change of discharging current density during discharge was found as follows:

When the resistance inserted in the circuit is small or when the discharge circuit is short-circuited, i) the discharging current density was high at early stage of discharge, ii) and in the course of time, it decreased rapidly and stepwise, iii) and finally after a definite time it reduced to approximately equal the discharging current density which was observed in the case where the resistor with 10 k ohms was inserted and the current density was led to stabilize. On the other hand, when the resistor with larger than 500 ohms was inserted, the current density was found to be low and in the course of time it decreased linearly very slowly. The status of the change of this discharge current density seemed to correspond to the status of change of de-

flection during discharge, which was shown already in Fig. 7.

## 6. Conclusion

The internal stress and the crystal structure of electrodeposited  $\text{PbO}_2$  from a lead nitrate bath were studied.

The results are summarized as follows:

1) The electrodeposited  $\text{PbO}_2$  deposited just after the start of electrolysis deflected in the direction of contraction in any case. When the electrolysis was carried out at  $10^\circ\text{C}$  and  $3 \text{ A/dm}^2$ , the deflection remained in the direction of contraction during the duration of electrolysis. When the electrolysis carried out at  $30^\circ\text{C}$  and  $3 \text{ A/dm}^2$  or at  $10^\circ\text{C}$  and  $1 \text{ A/dm}^2$ , the deflection changed in the direction of expansion during the duration of electrolysis.

2) The electrodeposited  $\text{PbO}_2$  which had access to the anode surface and the electrodeposited  $\text{PbO}_2$  which had kept the deflection in the direction of contraction until the end of electrolysis were both mainly  $\alpha\text{-PbO}_2$ . On the other hand, the surface of  $\text{PbO}_2$  which had changed deflection in the direction of expansion during the course of electrolysis was mainly  $\beta\text{-PbO}_2$ .

3) Either the  $\text{PbO}_2$  which had deflected in the direction of contraction during electrolysis or the  $\text{PbO}_2$  which had deflected in the direction of expansion during electrodeposition deflected in the direction of expansion on being held in air or in the bath. The rate of change of deflection in the same time interval of holding was larger for  $\alpha\text{-PbO}_2$  than for  $\beta\text{-PbO}_2$ .

4) Any of these electrodeposited  $\text{PbO}_2$  deflected in the direction of expansion during discharge. The rate and the magnitude of such deflection to expansion was larger as the discharge current density became higher, and the extent of this tendency became larger in the case of  $\alpha\text{-PbO}_2$  than in the case of  $\beta\text{-PbO}_2$ .

From the results of the above experiments with electrodeposited  $\text{PbO}_2$ , it can be concluded at least that the difference in crystal structure and the discharging current density are both important factors of the internal stress in the electrodeposited  $\text{PbO}_2$ .

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