

## 전해 이산화망간 제조에 관한 연구

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## A Study on the Preparation of Electrolytic Manganese Dioxide

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**요약.** 국산 rhodochrosite로부터 제조한 황산산성  $MnSO_4$  수용액을 전해산화하여 건전지용  $\gamma$ - $MnO_2$ 를 제조하는데에 관한 공업적 데이터를 얻기 위하여 하루에 4 kg의  $MnO_2$ 를 제조할 수 있는 micro pilot plant를 설치하여 실험하였다.

광석의 침출 및 전해산화 조건을 규명하고 제품의 물성을 화학분석, DTA, X-선회절, 전자 현미경 사진 및 전지방전 실험 등으로 검토하였다. 적합한 전해조건은 다음과 같다.

전해액의 온도:  $90^\circ C$  이상, 전류밀도:  $0.7 \sim 1 A/dm^2$ , 양극재료: 흑연 또는 납, 전해액의 농도:  $MnSO_4$  50~150g/l 및  $H_2SO_4/MnSO_4=0.15 \sim 0.25$ .

최적전해조건하에서 전류효율은 99% 이었고 생성된  $MnO_2$ 는 거의 순수한  $\gamma$ - $MnO_2$ 이었으며, 방전 특성은 우수하였다.

**Abstract.** With the intention of obtaining technical data for the industrial production of  $\gamma$ - $MnO_2$  for dry cell depolarizer by electrolytic oxidation of acidic manganese sulfate solution made from domestic rhodochrosite, optimum conditions of ore leaching, purification of leached solution and electrolytic oxidation of divalent manganese to tetravalent were investigated using simulated micro pilot plant having a production capacity of 4 kg of  $MnO_2$  per day.

The nature and quality of the products were investigated by means of chemical analysis, DTA, X-ray diffraction and electron microscopy. The cell activity of  $MnO_2$  were examined by cell discharging character measurements.

The optimum electrolysis conditions were as follow:

Temperature of the electrolyte, above  $90^\circ C$ ; current density,  $0.7 \sim 1 A/dm^2$ ; anode materials, graphite or lead; concentration of electrolyte,  $MnSO_4$  50~150 g/l and  $H_2SO_4/MnSO_4=0.15 \sim 0.25$ . Under the best condition the current efficiency was 99% and the products were almost pure  $\gamma$ - $MnO_2$ .

The cell discharging character were good and almost the same as that of regular grade commercial electrolytic manganese dioxide.

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### Introduction

The basic researches on the preparation of

electrolytic manganese dioxide (EMD) have been conducted by many authors e. g., Van Arsdale<sup>1</sup>, Nichols<sup>2</sup>, Vetter<sup>3</sup>, Muraki<sup>4</sup>, Era<sup>5</sup>, Kano<sup>6</sup>, Kim<sup>7</sup> and Glemser<sup>8</sup> etc. The influence of electrolytic conditions such as concentration of manganese sulfate and sulfuric acid, and of temp. of electrolyte and current density upon the current efficiency of the electrolysis were reported in detail, and the results there were in agreement with each other on the whole. However, the influence of electrolytic conditions upon the nature and quality of EMD has not yet been fully ascertained. Moreover papers on the industrial production of EMD are difficult to find. The purpose of this study was determination of optimum conditions of ore leaching and

purification of leached solution, finding the relationship between current efficiency and H<sub>2</sub>SO<sub>4</sub>/MnSO<sub>4</sub> molar ratio, investigation of the effect of anode materials, concentration and feeding rate of electrolyte on the quality of the EMD. And they were carried out with the use of a micro pilot plant installed in author's laboratory. The nature of the prepared EMD were also examined by means of chemical analysis, DTA, X-ray diffraction and electron microscopy. And the activity evaluation was made by cell discharging character measurement.

**Experimental**

**Materials.** Middle grade domestic rhodochrosite was pulverized to -100 mesh and used as

Table 1. Composition of the rhodochrosite ore employed

(1A)

Component	Mn	Ca	Mg	Al	Fe	Zn	Pb	SiO <sub>2</sub>	S
wt. %	28.5	4.8	3.1	0.2	2.32	0.07	trace	4.8	0.4

(1B)

Component	MnCO <sub>3</sub>	CaCO <sub>3</sub>	MgCO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	ZnCO <sub>3</sub>	SiO <sub>2</sub>
wt. %	60	12	10.5	0.4	3.4	0.14	4.8
Moles in 1kg of ore	5.2	1.2	1.3	0.04	0.2	0.01	0.8

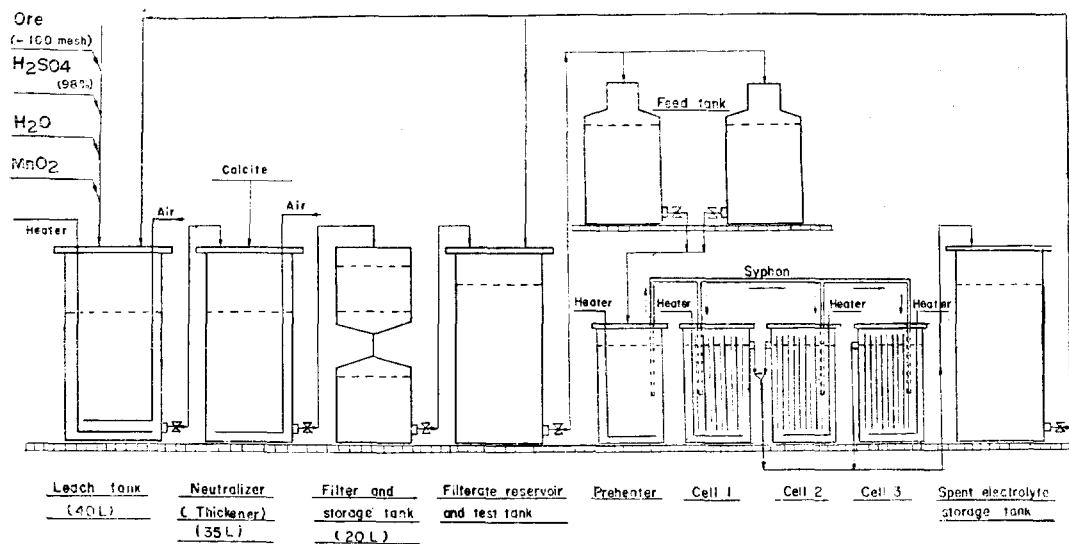


Fig. 1. Flow diagram for electrolytic manganese dioxide

starting raw material. The composition of the ore was shown in *Table 1*.

Sulfuric acid used for ore leaching was of commercial grade and fine powder of limestone was employed as neutralizing agent for acidic leached solutions.

**Equipments.** Assuming the production efficiency as 80~85%, a series of equipments for producing 4 kg of EMD per day was installed, and the layout is shown in *Fig. 1*.

As the structural materials of the equipments should stand against hot sulfuric acid solution and acidic fume, most of the vessels were coated with epoxy resin or lead sheet. The specification of principal equipments were as follows:

**Electrolytic cell:** Three 15×34.5×35 cm lead lined tank, 5 cm thick wood asbestos sandwiched wall. One of the cells were provided with a cover fitted with condenser for moisture and fume reflux.

**Anode:** Twelve 18×25×1.5 cm graphite sheets or 18×28×0.5 cm lead sheets.

Effective anode area: 12,810 cm<sup>2</sup>

**Cathode:** Fifteen 18.5×30×0.2 cm lead sheets, 12,960 cm<sup>2</sup> of effective area.

**Rectifier:** Silicon diode elements, 12 volts, 200 amp. capacity.

**Leaching and Purification.** Three kg of the ore was suspended in 22.4 l of water in the leaching tank, and there 1.35 l of 98% sulfuric acid was added with stirring. Heating and aeration were followed immediately and the temp. of slurry was kept above 80 °C for 5~7 hrs. At every hour of leaching, evaporated water was added and the concentration of manganese sulfate and sulfuric acid in the solution and that of manganese carbonate in the sludge were determined. After 95% of manganese had been leached, the slurry was neutralized with limestone powder to the pH of 6.2~6.6 and filtered. The Mn<sup>2+</sup> and impurities such as Fe<sup>2+</sup>, Fe<sup>3+</sup>,

Cu<sup>2+</sup>, Mg<sup>2+</sup> etc. in the filtrate were determined. To the sufficiently purified solution measured quantity of sulfuric acid or spent electrolyte was added to prepare desired electrolytes.

**Electrolysis.** It is well known that, the higher the temp. of electrolytes the higher current efficiency will be attained. In this experiment the temp. of electrolyte were kept at 90 ±2 °C. With the conditions tabulated in *Table 2* and 3 electrolysis was carried out for 120 hrs. at each run and evaporating water was supplemented continuously to each cell. As the electrolysis is taking place in large vessels and on many electrode surfaces, the actual concentration of the electrolyte differs with original or feeding electrolyte. Therefore, mean concentration of feeds and effluents of the cells was taken as actual concentration. After electrolysis, anodes with deposited EMD were rinsed in hot demineralized water several times and the EMD were stripped and pulverized to -200 mesh. The EMD was neutralized with 5% NaHCO<sub>3</sub> solution and washed again with hot water and dried at 100 °C.

**Quality Test of EMD.** Nature of the EMD were investigated by chemical analysis, DTA, Fe K $\alpha$  (no filter) X-ray diffraction and electron microscopy. The depolarizing character of the EMD was examined by cell discharging method in accordance with JIS<sup>9</sup> regulation in comparison with commercial EMD(T). All the cells tested were CM type which had specially made by commercial dry cell maker.

## Results and Discussion

**Leaching and Purification.** By single step leaching, similar to the method mentioned in previous section, 95% of leaching rate was obtained after 5 hrs. as seen in *Fig. 2*. This is equivalent to 755 g of manganese sulfate production from 1 kg of ore. At this point,

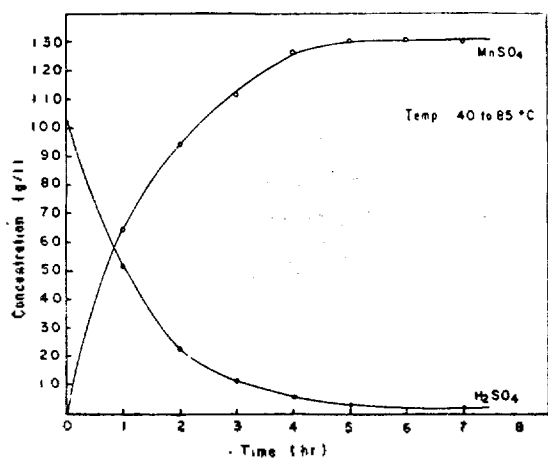


Fig. 2. Concentration of leached solution vs. time

by adjusting the pH of the solution to about 6.5 with limestone, almost all harmful impurities such as Fe<sup>3+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup> were precipitated as hydroxides or hydrated oxides and sufficiently purified by twice filtrations and no further purification was necessary.

**Current Efficiency.** Influence of H<sub>2</sub>SO<sub>4</sub>/MnSO<sub>4</sub> molar ratio of the electrolyte on the current efficiency is more important than single concentration effect of H<sub>2</sub>SO<sub>4</sub> or MnSO<sub>4</sub>. With the electrolyte concentration of 70~120 g/l of MnSO<sub>4</sub> and 16~99 g/l of H<sub>2</sub>SO<sub>4</sub>, the relation between the current efficiency and the molar ratio can be seen in Table 2 and Fig. 3. The

Table 2. Concentration of electrolytes and current efficiency

No. of run	H <sub>2</sub> SO <sub>4</sub> (mole/l)		MnSO <sub>4</sub> (mole/l)		Mean conc. of electrolytes in the cell during electrolysis				Molar ratio H <sub>2</sub> SO <sub>4</sub> /MnSO <sub>4</sub>	Current efficiency (%)
	Feed	Effluent	Feed	Effluent	H <sub>2</sub> SO <sub>4</sub>		MnSO <sub>4</sub>			
					(g/l)	(mole/l)	(g/l)	(mole/l)		
1	0.348	1.664	0.662	0.861	98.6	1.007	115.0	0.762	1.321	70.5
2	0.341	0.565	0.662	0.352	44.4	0.452	76.6	0.507	0.892	88.3
3	0.150	0.400	0.662	0.294	26.9	0.275	72.2	0.478	0.575	96.2
4	0.140	0.184	0.662	0.609	15.9	0.161	96.0	0.636	0.253	98.8

Table 3. Electrolysis conditions and current efficiency

MnO <sub>2</sub> designation	Electrolysis conditions						Current efficiency (%)
	Anode	D <sub>A</sub> (A/dm <sup>2</sup> )	H <sub>2</sub> SO <sub>4</sub> (g/l)	MnSO <sub>4</sub> (g/l)	Rate of feeding (l/hr)	Time of initial no feeding electrolysis (hr)	
A	C	1.0	66.8	108.7	6	0	86.4
B	C	1.0	98.6	115.0	5	0	70.5
C	C	1.5	145.6	151.5	4	0	60.5
D*	C	1.5	145.6	151.5	4	0	—
E	Pb	0.7	44.4	76.6	2	11	88.3
F**	Pb	0.7	44.4	76.6	2	11	88.3
G***	Pb	0.8	26.9	72.2	2	18	96.2
H	Pb	0.7	15.9	96.0	10	0	98.2
I	C	1.0	15.9	96.0	10	0	99.0

\* Dropped MnO<sub>2</sub> on the bottom of the C cell during electrolysis

\*\* Treated with 0.3% NH<sub>4</sub>Cl solution after neutralization

\*\*\* Covered cell

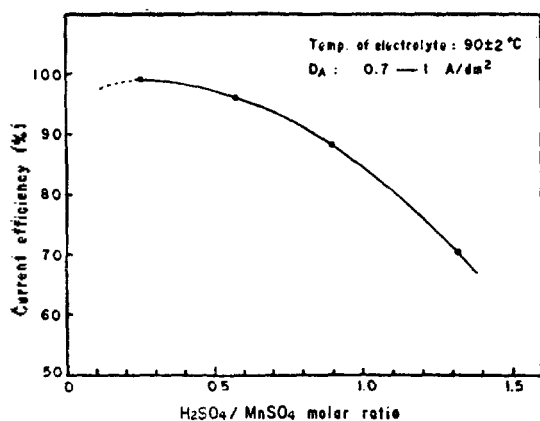


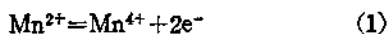
Fig. 3. Current efficiency vs. molar ratio

consequences of electrolysis conditions such as anode material, current density, concentration and feed rate of electrolyte are listed in Table 3.

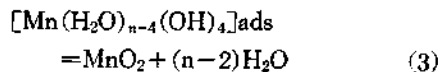
The feeding rate of the electrolyte did not appreciably effect on the current efficiency and quality of EMD. However, when heating of electrolytes are performed at outer part of the cell, e.g., heat exchanger and heater, rapid feeding is necessary to maintain the temp. of the electrolytes in the cell sufficiently high.

At the same current density, lead anodes displayed higher cell voltage than graphite anode, and even at the same voltage the EMD deposited on the lead anodes dropped off in sheet by itself.

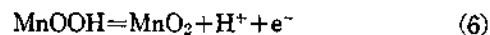
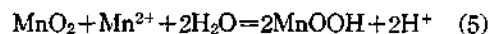
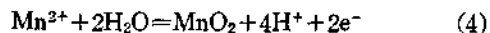
**Mechanism of the Electrolytic Oxidation of Manganese Sulfate.** Several investigators had proposed the mechanism of electrolytic oxidation of MnSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> aqueous solution to produce MnO<sub>2</sub>. Besides the Van Arsdale and Maier<sup>1</sup>, Geloso<sup>10</sup> and Kim<sup>7</sup> suggested that the anodic reaction would proceed in two steps as shown in eqs. (1) and (2), when the cell voltage and current density were low and temp. of electrolyte high.



Kim<sup>7</sup> also proposed that the rate determining step of the overall reaction was the second step, i.e., hydrolysis of Mn<sup>4+</sup>. Fleischmann<sup>11</sup> reported that the process of a intermediate, eq. (3), was the rate determining reaction.



On the other hand, Sugimori and Sekine<sup>12</sup> considered that the anodic reaction would proceed in three steps as shown in eqs. (4)~(6), and the electrochemical oxidation process of MnOOH, eq. (6), was the rate determining step.



Under the mild electrolysis conditions mentioned in previous section, it is clear that Mn<sup>4+</sup>, rather than Mn<sup>3+</sup>, is produced at the initial stage of electrolysis, by considering the standard reduction potentials<sup>13</sup>  $E^\circ_{\text{MnO}_2/\text{Mn}^{3+}} = 1.23$  volts,  $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}} = 1.51$  volts and analytical data of acting electrolyte. Due to the high positive charge density of Mn<sup>4+</sup>, it would be very unstable in aqueous solution. The evidence of high thermal dependence of the current efficiency is a direct testimony to a usual chemical reaction such as reaction (2) or (3) is the rate determining step of EMD production rather than electron transfer reaction.

The cathodic reaction is  $2\text{H}^+ + 2e^- = \text{H}_2$  for one mole of MnO<sub>2</sub> produced, and the overall reaction can be written as eq. (7). Therefore as the electrolysis proceeds the concentration of MnSO<sub>4</sub> decreases and that of H<sub>2</sub>SO<sub>4</sub> increases.

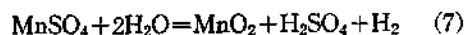
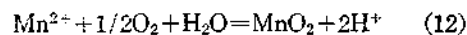
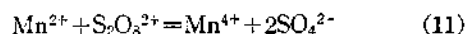
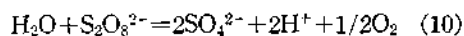
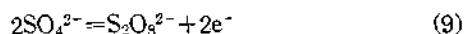
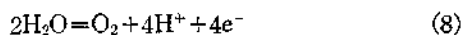


Table 4. Chemical compositions of the EMD (wt %)

MnO <sub>2</sub> sample designation	MnO <sub>2</sub>	H <sub>2</sub> O	Pb	Fe	Cu	SiO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	HCl insoluble matter	Bulk density	pH
A	91.17	2.17	0.26	0.034	Trace	0.16	1.84	3.25	1.02	1.5
B	91.50	2.31	0.24	0.038	Trace	0.17	1.47	2.01	1.16	2.0
C	83.31	1.04	0.32	0.024	—	—	1.59	8.79	0.91	2.0
D	77.27	6.88	4.68	0.181	Trace	2.36	6.46	4.54	0.94	1.2
E	93.90	1.28	0.80	0.081	Trace	0.16	2.07	0.37	0.91	1.6
F	91.34	3.27	0.69	0.062	—	—	0.99	0.79	0.89	1.9
G	90.21	2.51	0.17	0.044	Trace	1.00	0.75	1.28	0.72	5.1
H	91.29	3.93	0.15	0.043	—	—	0.45	0.48	0.85	3.9
I	89.54	3.00	0.05	0.022	—	—	0.82	4.26	0.78	3.6

In the industrial production of EMD, graphite or lead are usually employed as anode material as in this study. In these cases more than 2.2 volts of the cell voltage is necessary and under the conditions listed in Table 3 the cell voltage has developed as high as 2.5~2.8 volts. Such voltage increase is inevitable for high productivity.

From the point of view of the electrode potentials, side reactions such as eqs. (8)~(12) will take place at the anode and it undergoes oxidation by evolved oxygen.



This tendency is more remarkable when the temp. is low and concentration of sulfuric acid of the electrolyte is high.

**Compositions and DTA of EMD.** In Table 4 chemical compositions of the prepared EMD are shown. The lead contents of all of the EMD except sample I exceed the regulation of JIS and these lead contamination seems to be

resulted from lead cathode and cell lining. To minimize such lead contamination, electrolysis should be done in all graphite system. However, Era<sup>14</sup> et. al. reported that metallic or divalent lead contaminants would not exert negative effect on dry cell activity of EMD.

Sample D dropped from the electrode by itself during electrolysis at high current density and concentrated sulfuric acid electrolyte. It contained plenty of various impurities and manifested very low cell activity. Sample E and F also contained somewhat large quantity of iron owing to insufficiently purified electrolyte, and reflected upon their relatively low cell activity.

DTA curves of the EMD are shown in Fig. 4 en bloc. Both free and combined water of the EMD seem to have evolved below 370~380°C. According to Tvarusko<sup>15</sup>, elimination of free water and the combined water would take place until 110 and 400°C, respectively.

Sample D shows the highest decomp. temp. of the all, representing it has the most stable structure, and suggests it will exhibit the lowest activity. At about 460~580°C, and 940~990°C the decomp. of the EMD took place according to eqs. (13) and (14) respectively.

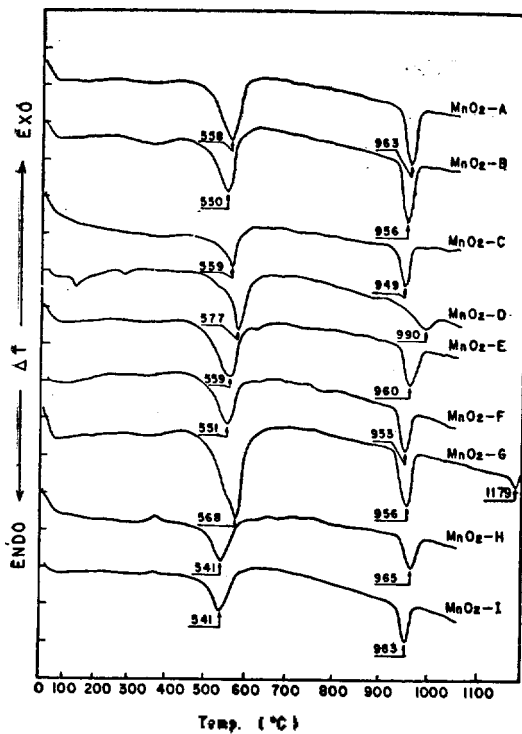
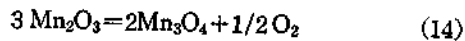
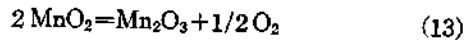


Fig. 4. DTA curve of the electrolytic manganese dioxides



#### X-ray Diffraction and Electron Microscopy

X-ray diffractograms of the EMD and a pyrolusite were lumped together in Fig. 5. All of EMD except D show the patterns agree with the ASTM card of the  $\gamma$ -MnO<sub>2</sub> on the whole. The pattern of sample D differs much from other EMD and the (110)<sup>16</sup> diffraction (at  $d=3.9\sim 4.1\text{\AA}$ ) almost disappears and shows pyrolusite ( $\beta$ -MnO<sub>2</sub>) like peak. There are many varieties of  $\gamma$ -MnO<sub>2</sub> characteristically having low crystallinity<sup>17</sup> in general, and particularly, electrolytic  $\gamma$ -MnO<sub>2</sub> gives less diffraction peaks than chemically prepared  $\gamma$ -MnO<sub>2</sub>. Although there is an exception, it seems that the intensities of the (110) diffractions represent the activities of EMD.

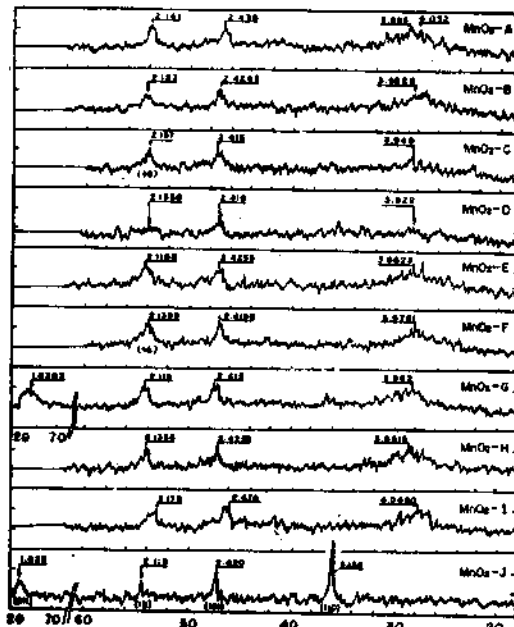


Fig. 5. X-ray diffractograms of electrolytic (A~I) and natural (J) manganese dioxide, FeK $\alpha$ (no filter) 30 kV, 10 mA

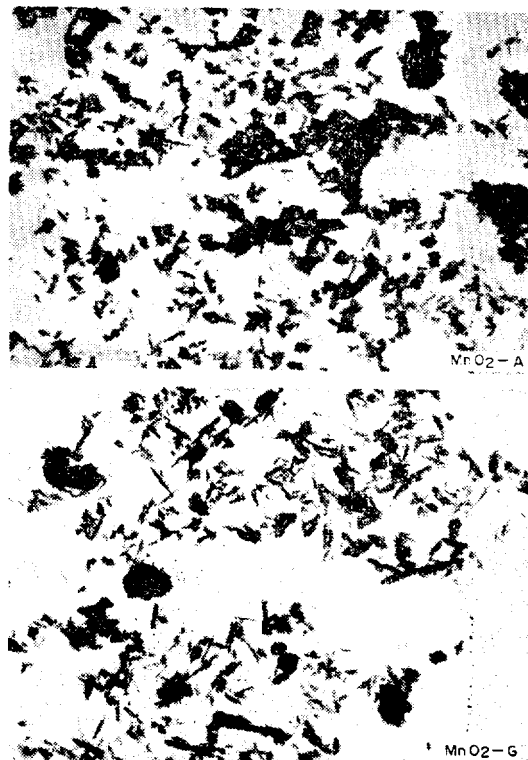


Fig. 6. Electron microscopic photo. of electrolytic manganese dioxides, double replica,  $\times 25,000$

Fig. 6 is electron microscopic photograph of two EMD magnified by 25,000 times and shows typical needle-like crystals of  $\gamma$ - $MnO_2$ .

**Cell Discharging Character.** The intermittent discharging life and self discharging character of the dry cells made from the prepared and an commercial EMD (T) are shown in Figs. 7 and 8. Among the samples listed in Table 4, the A, B, G, H and I displayed good cell activities, and D was the worst. The important factors influencing the cell activity of  $MnO_2$  are the amount of impurities such as iron and copper, and the structure of the  $MnO_2$ .

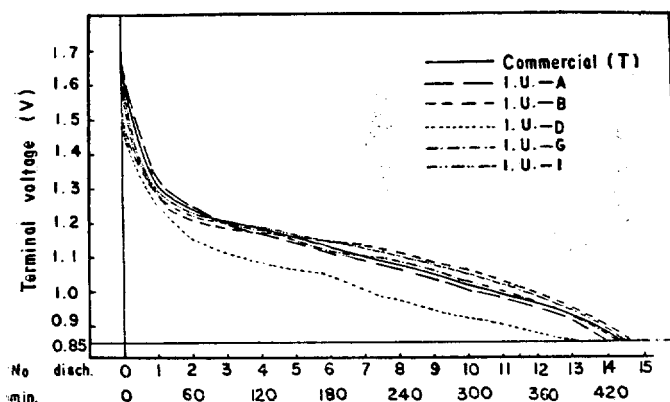


Fig. 7. Service life of the cells, intermittent discharge

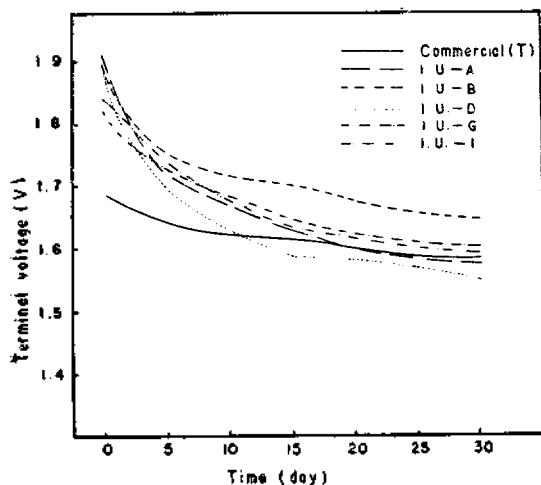


Fig. 8. Voltage drop owing to selfdischarge at 45°C

### Acknowledgement

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