

# STUDIES ON BATTERY ACTIVE PROPERTIES OF ELECTROLYTIC MANGANESE DIOXIDE CONTAINING IRON

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This paper records the observations made on the electro-deposition of manganese dioxide containing iron, and its battery active properties. The increase in iron content in the electrolyte resulted in an increase of Fe in  $\text{MnO}_2$  deposited, which was responsible for the increase in the electrode potential of the manganese dioxide samples. Manganese dioxide containing iron exhibited very small change in its potential on discharge. Also the rate of recovery was negligible compared to that of pure manganese dioxide. Moreover,  $\text{MnO}_2$  containing iron gave a comparatively high current and, unlike high purity electrolytic manganese dioxide and West African manganese ores, the fall in the current on discharge was very slow. These give favourable indications that the battery-activity of electrolytic  $\text{MnO}_2$  can be substantially improved by introducing Fe in  $\text{MnO}_2$ .

X-ray and thermal analysis did not show the presence of any other separate phase of iron, indicating that iron is co-deposited with  $\text{MnO}_2$ . This was further confirmed by neutron diffraction examination carried out at the Bhabha Atomic Research Centre. Attempts have been made to explain the observed results on the discharge characteristics, in the light of electron-proton mechanism.

## INTRODUCTION

Electrolytic manganese dioxide can be profitably used in dry cells where a good voltage and high current are required for a shorter period. At the same time, West African manganese dioxide ores are always preferred where a steady voltage and current are required for longer periods (Joseph *et al.* 1968). Detailed study of the West African manganese dioxide ore samples and electrolytic manganese dioxide showed that they are almost similar in chemical composition and basic structure (as revealed by the X-ray structure), except that the former contains impurities like Fe, Al, Cu and Si.

It is, therefore, quite natural to think that the presence of other metallic elements like iron and/or aluminium in the West African ores might be one of the factors responsible for their better performance in batteries, giving steady voltage and current for a longer period.

A few references are available where it has been reported that some changes in the lattice properties take place due to the presence of some foreign substances in  $\text{MnO}_2$  lattice (Schossberger 1941; Kozawa & Vosburgh 1958; Okada *et al.* 1947; and Cole *et al.* 1947). But systematic studies on electrolytic manganese dioxide,

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containing some foreign atoms, produced by electro-deposition from a solution containing foreign cations, is an unexplored region; no literature about the battery active properties of the electrolytic manganese dioxide containing co-deposited foreign atoms are available as far as the authors know.

#### MATERIALS AND METHODS

Electro-deposition of manganese dioxide was carried out from manganese sulphate-sulphuric acid bath. Chemicals used were C. P. grade manganese sulphate and A. R. quality  $H_2SO_4$ ,  $Ca(OH)_2$  and  $FeSO_4$ . Manganese sulphate solution was purified by adjusting the pH at 6.5 with the help of slaked lime followed by aeration. Activated charcoal was added to the bath to facilitate the separation of impurities. Electrolytes of different compositions were prepared from purified manganese sulphate solution, sulphuric acid and ferrous sulphate. In all cases, the manganese sulphate concentration was kept at 157–160 gms per litre.

The electrolysis was carried out using the technique already described by Chakrabarty and Banerjee (1953). Anodes and cathodes were graphite rods and platinum plates respectively. A continuous flow of the electrolyte was maintained through the bath at the rate of 6–8 ml per minute. The anodic deposition was carried out at 90–95°C and at a current density of 1.5 amp/cm<sup>2</sup>. The voltage applied was 2 volts.

After completion of electrolysis the anodes were washed, dried and weighed to determine the amount of deposit. The manganese dioxide was then either stripped off by mechanical scrapping or tested as such for determining their discharge characteristics. Iron, total manganese and manganese dioxide were chemically estimated using standard methods, such as total manganese by Volhard's method (Mellor & Thompson 1938), manganese dioxide by oxalate method and iron by spectrophotometric analysis.

*Current Efficiency*—Current efficiency was calculated using the following formula :

$$C.E. = \frac{26.8 \times 100 \times \text{wt. of deposited } MnO_2 \text{ (dried at } 120^\circ C)}{43.5 (\text{Eq. wt.}) \times \text{ampere} \times \text{hrs.}}$$

*Discharge and Recovery Characteristics*—The discharge of the  $MnO_2$  electrodes was carried out by short circuiting an amalgamated zinc rod and electrolytic  $MnO_2$  deposited on graphite in an electrolyte of 20 per cent  $NH_4Cl$  for 20 seconds, followed by measuring the electrode potential of the  $MnO_2$  electrode against a saturated calomel electrode. The discharge was carried out for a period of 12 minutes and, thereafter, the recovery characteristics in the potential of  $MnO_2$  electrodes were measured in the open circuit at an interval of five minutes. The recovery characteristics were observed on the whole for 70 minutes.

Long time discharge of the pure  $MnO_2$  and also of  $MnO_2$  containing iron was carried out with the same apparatus continuously till the potential of the electrode became zero with reference to the saturated calomel electrode. The current flowing through the closed circuit was measured with the help of a milliammeter.

*Structural Analysis*—X-ray diffraction analysis of the electro-deposits was carried out using powder photographic and diffractometric technique with unfiltered iron radiation.

Thermal analysis of the electro-deposits was carried out in a Derivatograph. Neutron diffraction analysis of manganese dioxide samples (containing iron, as deposited in the present investigation) was carried out at the Bhabha Atomic Research Centre.

### EXPERIMENTAL RESULTS

#### 1. Analysis of a Sample of West African Ore ( $Mn_1$ ) :

(a) This analysis used in this investigation, indicated its  $MnO_2$  and Fe contents as 80.10 per cent and 1.76 per cent respectively.

#### 2. Effect of Iron Content on Electrolytic $MnO_2$ :

(a) Increase in the iron content in the electrolytic bath showed an increase of iron in  $MnO_2$ . The presence of  $Fe^{++}$  in the bath had a marked decreasing effect on current efficiency, reaching a value of 0.7 per cent at Fe concentration of 8.2 gms/litre (see Table I).

(b) Electrode potential developed by electro-deposited  $MnO_2$  containing Fe showed a general increase with the increase in its Fe content (see Table I).

TABLE I

*Effect of Iron in the Electrolyte on Electro-deposited Manganese Dioxide*

Sample No.	Conc. of Fe in electrolyte gm/lit	Yield in (gms)	Current efficiency %	Conc. of Fe in $MnO_2$ (wt. %)	Initial electrode pot. against $H_2$ electrode (volts)
A1	0.00	7.011	108.0	0.00	1.015
A8	0.78	5.173	79.6	2.57	1.1475
A7	1.50	3.50	54.0	4.58	1.1245
A6	2.42	0.798	12.0	6.18	1.2545
A4	6.27	0.28	3.4	5.64	1.1715
A5	8.27	0.048	0.729	6.16	1.2695

#### 3. Discharge and Recovery Characteristics :

The results obtained from the study of the discharge and recovery characteristics of different manganese dioxide electrodes are illustrated in Fig. 1.

Fig. 1 shows that the rate of discharge was very rapid in the case of electrodes, prepared from electrolytic  $MnO_2$  containing no iron. In this case the rate of recovery, after discharge for a period of 12 minutes, was equally very rapid in the initial stage but soon attained more or less a constant value. The West African variety showed a slower and steadier rate of discharge and also a comparatively slower rate of recovery. But the discharge curves of electrolytic manganese dioxide containing iron in various amounts showed a sharp departure from that observed with the samples containing no iron. These samples exhibited very small change

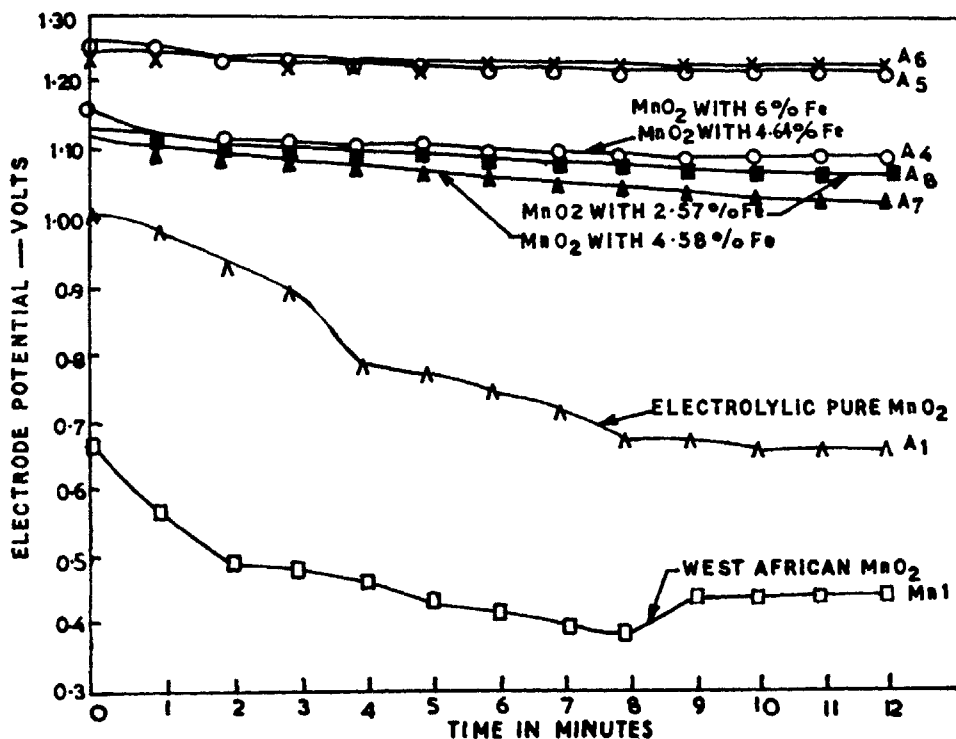


FIG. 1. Discharge of  $\text{MnO}_2$  electrodes containing iron (Electrode Potential against Time)

in their potential on discharge and the rate of recovery was also negligible when compared with that of pure electrolytic manganese dioxide.

The results obtained for the discharge of the electrode for sixty minutes are plotted in Fig. 2. The nature of the curves for pure electrolytic  $\text{MnO}_2$  and West African ore are more or less similar except that pure  $\text{MnO}_2$  showed a very high current in the initial stage of discharge. Manganese dioxide containing iron, on the other hand, showed a comparatively very high current and the fall in the current on discharge was very slow.

#### 4. Thermal and X-ray Diffraction Studies :

- X-ray diffraction results (d-value along with intensities) of  $\text{MnO}_2$  samples containing iron along with those of pure  $\text{MnO}_2$  and West African ores are given in Table II. The X-ray powder diffraction patterns of electrolytic  $\text{MnO}_2$  with and without iron showed broad and diffused lines, which were similar to  $\gamma\text{-MnO}_2$  though some differences were noted in the diffraction pattern.
- Differential thermal analysis of  $\text{MnO}_2$  samples containing iron and that of pure  $\text{MnO}_2$  showed three endothermic peaks near  $150^\circ\text{C}$ ,  $540^\circ\text{C}$  and  $980^\circ\text{C}$  which correspond to the evolution of water, conversion to  $\text{Mn}_2\text{O}_3$  and

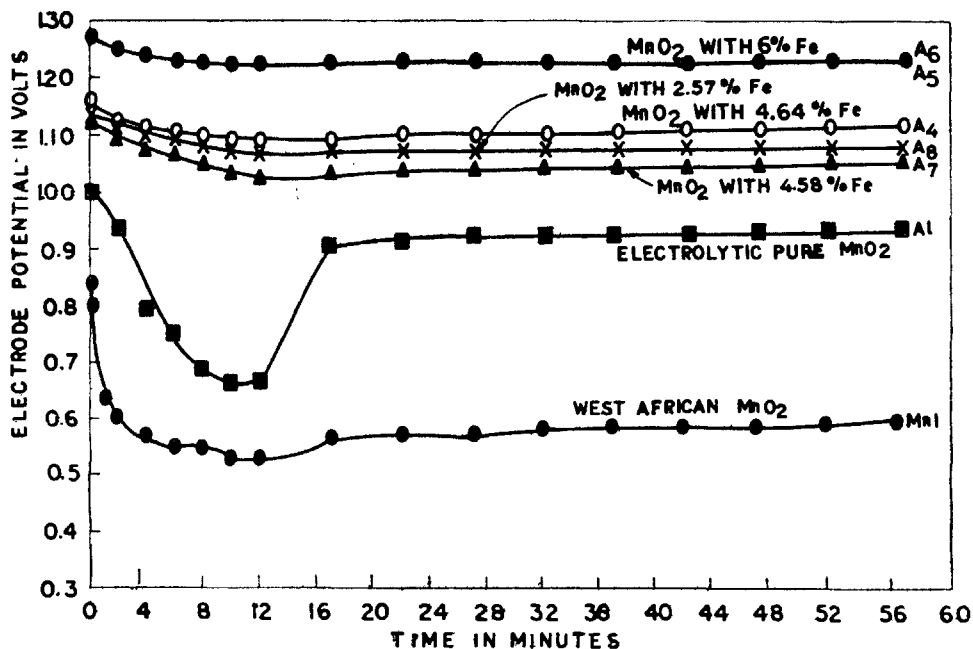


FIG. 2. Discharge and recovery of MnO<sub>2</sub> electrodes containing iron (Electrode Potential against Time)

reduction to Mn<sub>3</sub>O<sub>4</sub> respectively, the phase transformations being confirmed by X-ray diffraction examination (see Table III). With iron containing MnO<sub>2</sub> transformations to Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> occurred at slightly higher temperatures than that of pure MnO<sub>2</sub>. While the transformations in case of pure MnO<sub>2</sub> showed clear and smooth changes, indicated by comparatively sharp rise in peaks, MnO<sub>2</sub> samples, containing Fe, gave a flat peak indicating that these changes take place over wider ranges of temperature.

#### DISCUSSION

The salient features of electro-deposited manganese dioxide from electrolytic bath containing sulphate of iron besides manganese sulphate and sulphuric acid have been given as items 2-4 under experimental results.

*X-ray diffraction pattern*—Differences in the pattern (see Table II) obtained for  $\gamma$ -MnO<sub>2</sub> have also been reported by other workers (Cole *et al.* 1947; and Feitknecht & Marti 1945). According to Dubois (1936) and Schossberger (1941), these differences are due to the differences in the method of preparation and can be attributed to lattice distortion or defect brought about by the foreign ions or anion vacancy (MnO<sub>1.8</sub>). The pattern obtained in the present work resembled the one, reported by Cole *et al.* (1947), who identified three different forms of  $\gamma$ -MnO<sub>2</sub> in electrolytic MnO<sub>2</sub>, one of which is to some extent similar to West African ores. The other two types do not resemble natural products and form a transition between a tetragonal

TABLE II  
X-ray diffraction results of electrolytic  $MnO_2$  containing Iron

West African ore d--A/I/Io	Electrolytic pure Al d--A I/Io	A8 (2.57% Fe) d--A I/Io	A7 (4.58% Fe) d--A I/Io	A6 (6.18% Fe) d--A I/Io	$\gamma MnO_2$ Cole (1947) d--A I/Io	$\gamma MnO_2$ Cole (1947) d--A I/Io	Ramsdellite Cole (1947) d--A I/Io
4.01 (S)	4.36 (S)	3.96 (S)	3.91 (S)	4.06 (S)	4.38 (S)	4.38 (S)	4.05 (VS)
3.74 (S)	3.82 (S)				3.82 (MS)		
3.38 (S)					3.10 (W)		
3.135 (M)					2.68 (W)		3.12 (S)
2.597 (M)							
2.454 (M)							
2.363 (S)	2.391 (S)	2.424 (S)	2.43 (S)		2.57 (W)		2.53 (MS)
2.152 (S)	2.134 (S)	2.130 (S)	2.13 (S)	2.137 (S)	2.42 (MS)	2.42 (MS)	2.41 (MS)
1.828 (M)					2.34 (W)	2.34 (W)	2.33 (M)
					2.12 (S)	2.12 (S)	2.13 (M)
					2.05 (W)	2.05 (W)	2.10 (VW)
1.650 (S)	1.639 (MB)	1.65 (MB)	1.652 (MB)	1.644 (MB)	1.63 (S)	1.63 (S)	1.95 (W)
1.438	1.563 (W)						1.89 (VWV)
	1.476 (W)						1.81 (VWV)
1.343 (M)	1.394 (W)	1.41 (M)	1.412 (M)	1.407 (MB)	1.59 W	1.59 W	1.65 (MS)
	1.333 (M)				1.43 (VW)	1.43 (VW)	1.61 (S)
					1.35 (VW)	1.35 (VW)	1.55 (VW)
					1.31 (VW)	1.31 (VW)	1.53 (VW)
1.291 (W)							1.47 (M)
	1.202 (S)						
	1.124 (W)						1.42 (M)
							1.351 (MS)

S — Strong, M — Medium, W — Weak etc.

TABLE III

*X-ray Diffraction Results of Manganese Dioxide, Heat-treated to Various Temperature*

Samples	Heat treatment	Phase identified by x-ray diffraction
West African ore	350°C/24 hrs	Pyrolusite ( $\beta$ -MnO <sub>2</sub> )
	450°C/24 hrs	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub> , $\gamma$ -Mn <sub>2</sub> O <sub>3</sub>
	595°C/½ hr	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub> , $\gamma$ -Mn <sub>2</sub> O <sub>3</sub>
	980°C/½ hr	Mn <sub>3</sub> O <sub>4</sub>
Electrolytic pure MnO <sub>2</sub>	350°C/24 hrs	Pyrolusite ( $\beta$ -MnO <sub>2</sub> )
	450°C/24 hrs	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub> and Bixibite
	535°C/½ hr	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub> , $\gamma$ -Mn <sub>2</sub> O <sub>3</sub>
	970°C/½ hr	Mn <sub>3</sub> O <sub>4</sub>
Electrolytic MnO <sub>2</sub> (containing iron)	350°C/24 hrs	Pyrolusite ( $\beta$ -MnO <sub>2</sub> )
	450°C/24 hrs	$\gamma$ -Mn <sub>2</sub> O <sub>3</sub> , $\alpha$ -Mn <sub>2</sub> O <sub>3</sub>
	535°C/½ hr	Bixibite, $\gamma$ -Mn <sub>2</sub> O <sub>3</sub>
	1010°C/½ hr	Mn <sub>3</sub> O <sub>4</sub>

pyrolusite to orthorhombic ramsdellite structures. Present results on powder diffraction analysis of the electrolytic pure MnO<sub>2</sub> and those containing lower amounts of iron showed that they mostly resemble the  $\gamma$ -MnO<sub>2</sub>' type as described by Cole *et al.* (1947), except for sample A8 containing 2.57 per cent Fe; some of the weak lines are, however, absent. Results of Dubois (1936) and Glemser (1939) are also similar in many respects. MnO<sub>2</sub> containing 4.6 and 6.2 per cent Fe are again similar to A8 and resemble the type of  $\gamma$ MnO<sub>2</sub>' described by the same authors. Despite these differences no systematic changes have been noted in the X-ray diffraction patterns of MnO<sub>2</sub> containing different amounts of Fe. It may, however, be mentioned that the presence of Fe has not been accounted for in any of the patterns as a separate phase in any form of its compounds. Neutron diffraction analysis of MnO<sub>2</sub> containing Fe (as prepared by electro-deposition in the present investigation), carried out at the Bhabha Atomic Research Centre, also revealed that iron had entered into the MnO<sub>2</sub> lattice. The iron atoms either occupied lattice sites by replacing Mn atoms or they have entered into the interstitial positions. The possible effects of the presence of Fe atoms on the X-ray diffraction have been indicated by the broad and diffused nature of the lines due to close similarity in the X-ray scattering power of Fe and Mn atoms.

*Thermal Studies*—The observations made in the present investigation on high temperature transformations (*see* Table III) indicate that the presence of Fe in MnO<sub>2</sub> lattice affects the transformation characteristics of MnO<sub>2</sub> by making it more sluggish. It appears that Fe in MnO<sub>2</sub> lattice is transferred to Mn<sub>2</sub>O<sub>3</sub> or Mn<sub>3</sub>O<sub>4</sub> lattice and this process cause a lag in transformations, requiring higher energy *i.e.*, temperature and time which explains the broad nature of the peak, obtained in Derivatographs.

## MECHANISM OF ELECTRO DEPOSITION AND ELECTROCHEMICAL FEATURES

*Mechanism of Electro-deposition*

In the present studies electrolytic manganese dioxide co-deposited with iron did not show the presence of any other separate phase of iron as determined by X-ray and thermal analysis. X-ray pattern showed, as mentioned before, the presence of  $\gamma\text{-MnO}_2$ , indicating that iron is co-deposited along with  $\text{MnO}_2$ . Neutron diffraction examination, carried out at the Bhabha Atomic Research Centre confirmed the above observation. Chakrabarty and Banerjee (1960) have discussed in detail the various steps involved in the anodic oxidation of  $\text{Mn}^{2+}$  to form  $\text{MnO}_2$ .

The abnormal anodic current efficiency of 108 per cent can be explained on the basis of one molecule of water being incorporated with two molecules of  $\text{MnO}_2$  (Chakrabarty & Banerjee 1953). The current efficiency of electro-deposition of manganese dioxide decreases with the increase in the concentration of ferrous iron in the electrolytic bath. The standard oxidation-reduction potential of  $\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}}$  is  $-0.771$  compared to  $-1.28$  for  $\frac{\text{Mn}^{2+}}{\text{Mn}^{4+}}$ . In presence of ferrous iron in the bath,  $\text{Fe}^{2+}$  will also be oxidised to  $\text{Fe}^{3+}$  at the anode and find a place in the manganese dioxide lattice. When the concentration of ferrous iron in the electrolyte increases, some of the  $\text{Fe}^{3+}$  ions already formed by oxidation, may also get a chance to be reduced again at the cathode, regenerating  $\text{Fe}^{2+}$  which, in turn, may again get oxidised at the anode, thus bringing in a greater decrease in the overall current efficiency of the process.

*Observations on Discharge Characteristics*—It has been suggested by several workers (Vosburgh 1959; Ferrell & Vosburgh 1951; Colemann 1946; Kozawa and Yeagar 1965; and Kornfeil 1962) that lattice of electrolytic manganese does not contain only manganese ion in the tetravalent state but some of the trivalent  $\text{Mn}^{3+}$  ions are also present in it. The electrode potential of manganese dioxide has been attributed to the potential generating mechanism of the homogeneous phase  $\text{Mn}^{3+}\text{—Mn}^{4+}\text{—O}''\text{—OH}''$  phase (Kozawa & Powers 1966) in contact with an electrolyte, which is somewhat analogous to an aqueous redox system and the potential can be expressed by the equation :

$$E = E_0 - \frac{RT}{F} \log \frac{\text{Mn}^{3+} \text{ solid}}{\text{Mn}^{4+} \text{ solid}} \quad (1)$$

In the present system  $\text{Mn}^{4+}\text{—Mn}^{3+}\text{—Fe}^{3+}\text{—O}''\text{—OH}'$  some of the  $\text{Mn}^{3+}$  ions may be supposed to be replaced by  $\text{Fe}^{3+}$  ions in  $\text{MnO}_2$  lattice. This obviously reduces the concentration of  $\text{Mn}^{3+}$  in the  $\text{MnO}_2$  electrode resulting in an increased electrode potential of the manganese dioxide. This explains the increase in the electrode potential of manganese dioxide with the increase in its iron content (Table I).

Fig. 3 shows that the rate of discharge of manganese dioxide electrode containing iron is slower than that observed with pure electrolytic manganese dioxide. It can be seen from Fig. 3 that, after a period of 40 minutes of discharge, the electrode potential of electrolytic manganese dioxide containing iron is about 0.6 volt with calomel as the reference electrode or 0.8 volts with reference to hydrogen electrode.



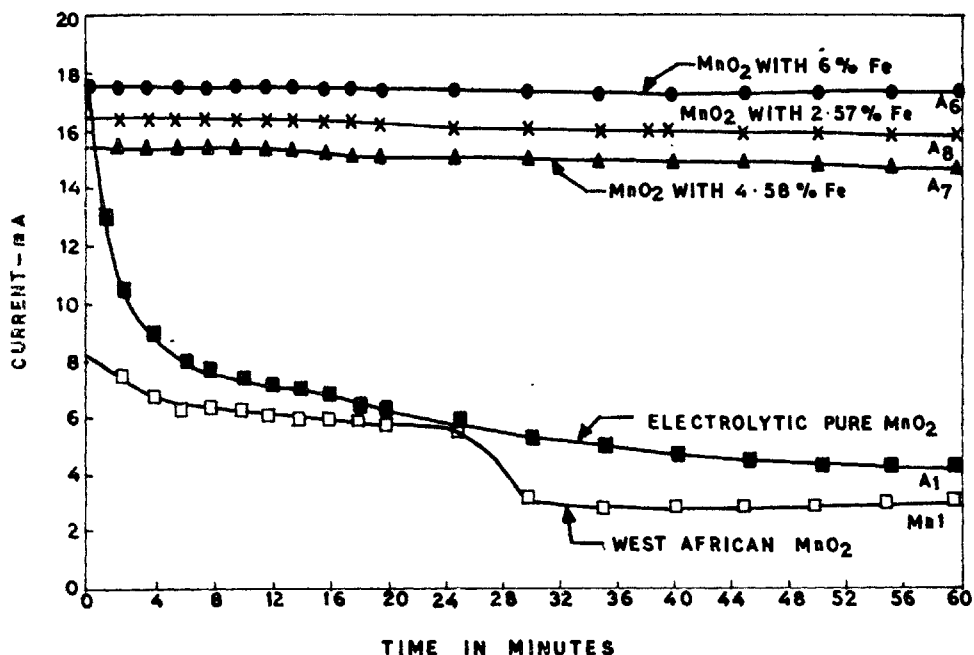


FIG. 3. Discharge of MnO<sub>2</sub> electrodes containing iron (Current against Time)

The reduction potential of the system  $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$  is 0.771 volts. It may, therefore, be concluded that at this stage of discharge of the MnO<sub>2</sub> electrode, the usual reduction of Mn<sup>4+</sup> to Mn<sup>3+</sup> is accompanied by reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> with the result that the rate of discharge of the electrode become slow without affecting much the supply of energy (current) from the electrode. This cannot, however, be said for pure MnO<sub>2</sub> electrode, where, as expected, discharge rate is appreciably much higher.

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