

## Rechargeability of manganese dioxide/zinc cell using zinc sulfate electrolyte

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### Abstract

The charge/discharge of electrolytic  $\gamma$ - $\text{MnO}_2$  (EMD) in sulfate solution rather than chloride was investigated. Discharge potential–time curves at different conditions of current density, charging schemes and solutions were registered. The charge/discharge cycle can be repeated up to the 20th cycle with no significant change in the discharge behaviour. The charge/discharge products are characterized by X-ray diffraction pattern indicating recovery of  $\gamma$ - $\text{MnO}_2$  during charging process. The results are promising and encouraging. They are discussed in the light of recent views.

### Introduction

Recharging of Leclanché-type cells has not been successful [1] primarily because the occurrence of irreversible reactions in the manganese dioxide/ammonium chloride/zinc system presented problems that could not be solved.

In the early 1950s efforts were commenced to make primary alkaline cells rechargeable [2–13], and to overcome the limitation of the discharge of  $\text{MnO}_2$  to its first electron only; as it is known [14–16] that  $\text{Mn(II)}$  is not rechargeable under battery conditions, less attention has been focused on rechargeability of  $\text{MnO}_2$  cells in acid and neutral media.

The present work concerns the charge/discharge of  $\text{MnO}_2$  in zinc sulfate solutions as acid medium. Some publications have appeared recently on this subject [17, 18]. It is one of a series on rechargeable zinc/manganese dioxide cells that are taking over recently, and are commercially produced on a large scale.

### Experimental

The  $\text{MnO}_2$  under investigation was of  $\gamma$ -type prepared electrolytically as previously described [19], and identified by X-ray diffraction (XRD). The cathode mixture consisted of  $\gamma$ - $\text{MnO}_2$  with acetylene black (20%). The anode was made of a pure-zinc sheet (99.99%). The electrolyte was 1 M zinc sulfate or zinc chloride of analytical grade. The cell used was described elsewhere [20] and all measurements were carried out at room temperature.

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The cell was discharged at 15 mA/0.5 g cathodic mixture until the cutoff voltage of 0 V versus saturated calomel electrode (SCE). Recharging of the cell at different constant currents (0.5–20 mA/electrode) for varying periods of time (1–60 h) was repeated for several cycles. The products removed from the test cell were washed with distilled water, dried at 80 °C and characterized by XRD.

## Results and discussions

Figure 1 shows the discharge potential–time ( $E-t$ ) curves for  $\gamma$ -electrolytic  $\text{MnO}_2$  at constant current of 15 mA/0.5 g cathodic mixture in 1 M  $\text{ZnSO}_4$  and 1 M  $\text{ZnCl}_2$ , respectively. The discharge continued to 0 V versus SCE, corresponding to a cell voltage of 1 V. The discharge capacity of the cell in sulfate solution was 89.5% of that of the capacity in  $\text{ZnCl}_2$  solution as calculated from the discharge time.

The slope of the discharge curve in  $\text{ZnSO}_4$  solution is typical for Leclanché cell ( $\text{ZnCl}_2$  electrolyte) as the reduction of  $\text{MnO}_2$  is characterized by a homogeneous phase reaction.

### Charge/discharge cycling

Figure 2 shows the repeated charge/discharge behaviour of  $\gamma\text{-MnO}_2$  in 1 M  $\text{ZnCl}_2$ . The cell was first discharged at 15 mA/0.5 g cathodic mixture (first cycle). It was then recharged at 2 mA/electrode for 20 h and subsequently discharged at 10 mA/0.5 g electrolyte (second cycle). A similar charge and discharge procedure was carried out (third cycle). It is clear from the Figure that a progressive decrease of cell voltage is observed at any value of discharge time, especially towards the end of discharge. The time of discharge also steadily decreased. The coulombic efficiency at the third cycle was 72.5% of that of the first cycle. This finding shows the quick failure of a  $\gamma\text{-MnO}_2/\text{ZnCl}_2/\text{Zn}$  cell, if it is cycled.

On the other hand, a sample of  $\gamma\text{-MnO}_2$  was first discharged at 15 mA/0.5 g cathodic mixture then left to recuperate overnight. It was charged at 20 mA/0.5 g

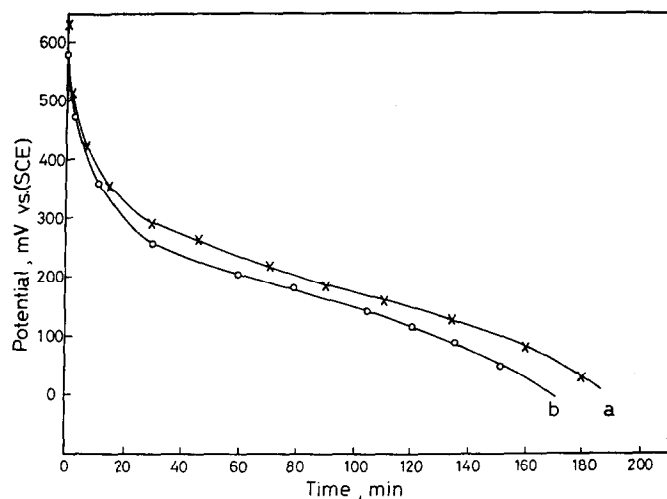


Fig. 1. Discharge curves of  $\gamma\text{-MnO}_2$  at 15 mA/0.5 g: (a) 1 M  $\text{ZnCl}_2$ , and (b) 1 M  $\text{ZnSO}_4$ .

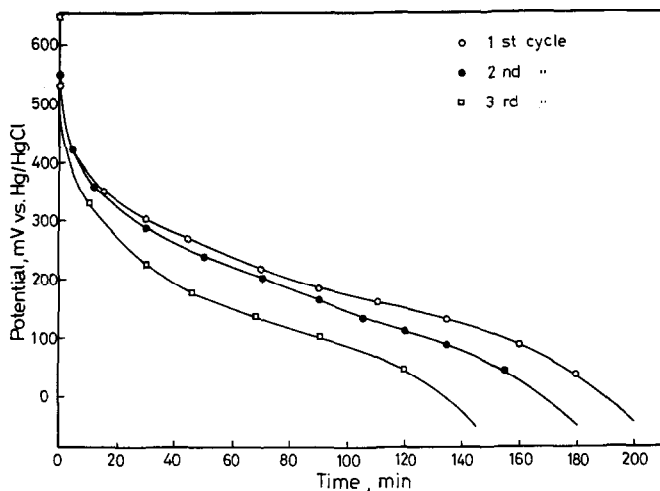


Fig. 2. Charge/discharge cycle of  $\gamma$ - $\text{MnO}_2$  at 15 mA/0.5 g in 1 M  $\text{ZnCl}_2$ .

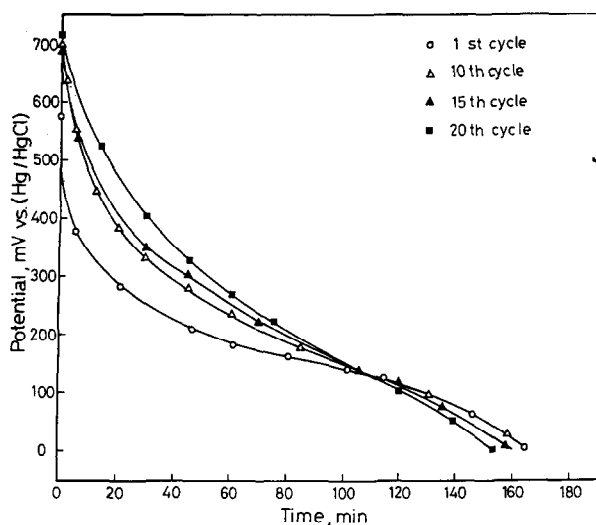


Fig. 3. Charge/discharge cycle of  $\gamma$ - $\text{MnO}_2$  at 15 mA/0.5 g in 1 M  $\text{ZnSO}_4$ .

cathodic mixture for 1 h, then discharged at 15 mA/0.5 g cathodic mixture. The cycle of recuperation charging and discharging was repeated for more than 20 cycles. The results are shown in Fig. 3. This Figure reveals a progressive increment of the 'starting' potential and cell voltage of discharge times up to 100 min after which low values of cell voltage were recorded. No significant change in coulombic efficiency was observed.

$\text{MnO}_2$  is reduced in a homogeneous phase reaction [21] and its potential decreases gradually as the discharge proceeds. The electrode potential is determined by the distribution of  $\text{Mn(III)}$  and  $\text{Mn(IV)}$ , whereby the ratio of the two Mn species determines the state of reduction and the shape of the discharge curve:



There is a general consensus [21, 22] that the cathodic reduction of  $\text{MnO}_2$  proceeds via a solid-solution reaction involving injection of protons into the  $\text{MnO}_2$  crystal lattice.

Reversible reduction occurs from  $\text{MnO}_2$  to about  $\text{MnO}_{1.7}$  [23], after which, further reduction results in irreversible changes in the structure and composition. The previous results in  $\text{ZnCl}_2$  and  $\text{ZnSO}_4$  are strictly confined to the region of the one-electron discharge of  $\text{MnO}_2$ , yet a large difference is observed between the two media. This behaviour, the possibility of repeated charge/discharge of  $\gamma\text{-MnO}_2$ , may well be attributed to the sulfate ion [18]. It was confirmed that the oxidation/reduction of  $\text{Mn}^{2+}/\text{Mn}^{4+}$  showed good reversibility in 1 N  $\text{H}_2\text{SO}_4$  but not in 1 N HCl solution.

To check the phases that may be formed, the XRD of the reference electrolytic  $\gamma\text{-MnO}_2$  was registered (curve a, Fig. 4). A discharged sample, as usual, was also checked by XRD (curve b). Additional lines appeared that may be ascribed to the formation of  $\text{MnOOH}$  during the reduction of  $\gamma\text{-MnO}_2$ .

Other samples were charged even for 20 h; curve c did not show a clear XRD of degenerated  $\gamma\text{-MnO}_2$  may be due to incomplete oxidation. Hence, another sample was discharged as usual, then slowly recharged at 2 mA/0.5 g cathodic mixture for 60 h; the XRD is revealed by curve d, Fig. 4, which was very encouraging as it was

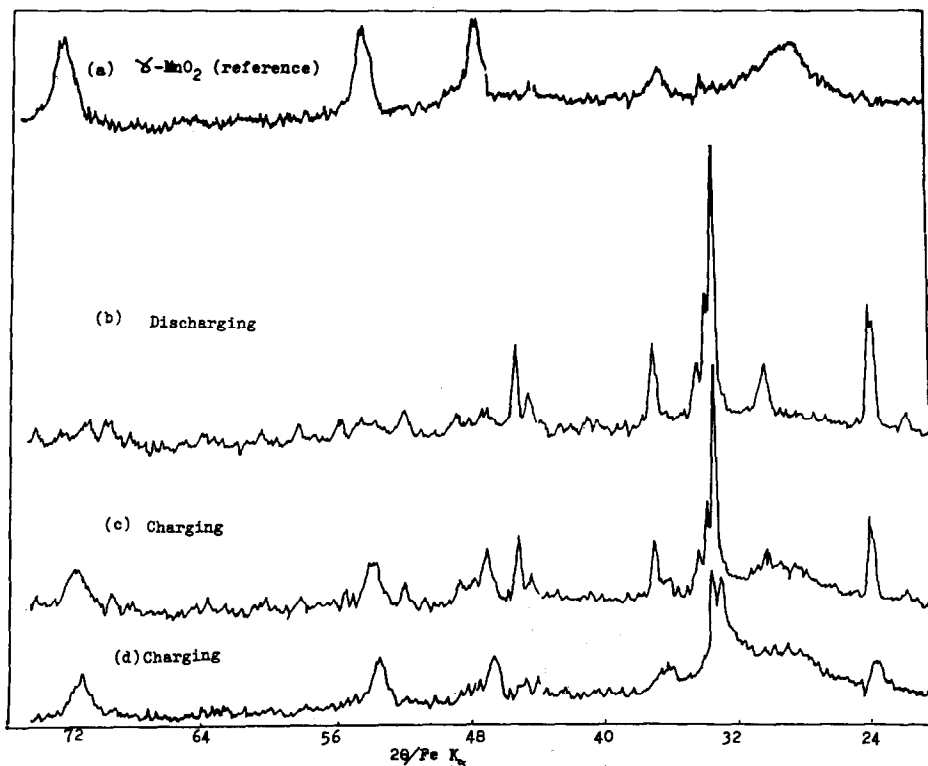


Fig. 4. X-Ray diffraction patterns of charged/discharged samples. (a) reference sample ( $\gamma\text{-MnO}_2$ ); (b) reference sample after discharge; (c) sample (b) at 2 mA/electrode for 20 h, and (d) sample (b) at 2 mA/electrode for 60 h.

close to the XRD of the reference sample (curve a). The lines were slightly shifted from those of the reference sample. This fact may be attributed to the fact that this electrochemical conversion of the discharged phases back to  $\gamma\text{-MnO}_2$  in the cell has entirely different electrochemical reaction conditions as compared with the originally produced electrolytic reference  $\gamma\text{-MnO}_2$ .

#### Effect of charging current on the discharge capacity

Three samples of  $\gamma\text{-MnO}_2$  were discharged at 15 mA/0.5 g cathodic mixture to the cutoff voltage (0 V versus SCE), then recharged for 20 h at 0.5, 1 and 1.3 mA/0.5 g cathodic mixture, respectively. Each sample was discharged at 15 mA/0.5 g cathodic mixture. The results are illustrated in Fig. 5 and given in Table 1.

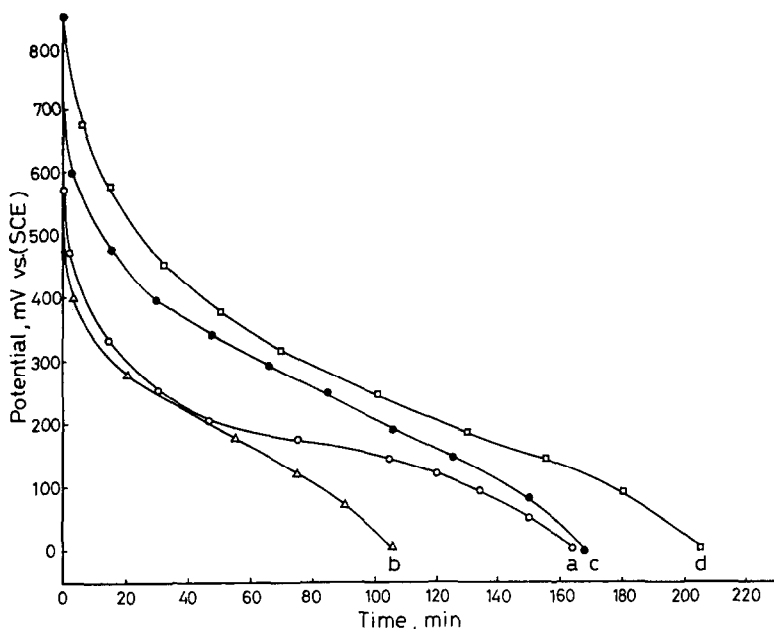


Fig. 5. Effect of charging current on the discharged samples: (a) reference sample; (b) charged at 0.5 mA/0.5 g cathodic mixture; (c) charged at 1 mA/0.5 g cathodic mixture, and (d) charged at 1.3 mA/0.5 g cathodic mixture.

TABLE 1

Effect of charging current on discharge capacity

No.	Charging current (mA/electrode)	Open-circuit potential (V)	Discharge time (min)	Coulombic efficiency compared with reference (%)
1	reference sample	600	165	
2	0.5	575	105	63.6
3	1.0	850	168	101.8
4	1.3	1100	205	124.2

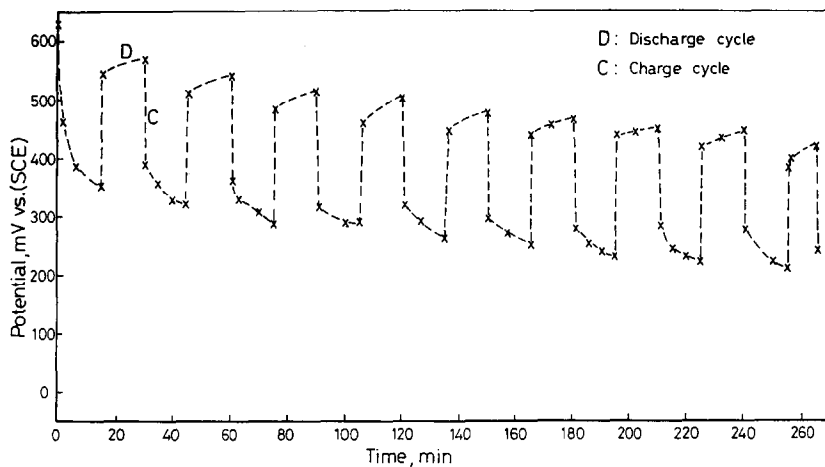


Fig. 6. Shallow charge/discharge cycles of  $\gamma$ - $\text{MnO}_2$  at 15 mA/0.5 g mix in 1 M  $\text{ZnSO}_4$ .

It was noticed that when the charging current was 0.5 mA/0.5 g cathodic mixture, the open-circuit potential and the discharge time were less than the reference sample. The coulombic efficiency was only 63.6% compared with the reference sample. This clearly denotes an incomplete charging of the sample. But as the charging current was  $> 1$  mA/0.5 g cathodic mixture, the open-circuit potential was progressively increased, and higher potential values were acquired throughout the discharge as seen in Fig. 5. The coulombic efficiencies exceeded 100% compared with the reference sample as given in Table 1.

Shallow cycling of a  $\text{MnO}_2/1$  M  $\text{ZnSO}_4/\text{Zn}$  cell was also investigated. The cell was discharged for 15 min at 15 mA/0.5 g cathodic mixture, then recharged for another 15 min at the same current and so on. This cycle was repeated more than 10 times. Figure 6 shows the curve obtained, the cell showed a good behaviour. No tendency of cell failure was noticed, yet a slight gradual decrease in the values of potential recorded just before the beginning of discharge was observed. Shallow cycling of a  $\text{MnO}_2/2$  M  $(\text{NH}_4)_2\text{SO}_4/\text{Zn}$  cell showed rechargeability [18], but the zinc anode deteriorated quickly.

The foregoing results suggested the possibility of producing a rechargeable  $\gamma$ - $\text{MnO}_2/\text{ZnSO}_4/\text{Zn}$  secondary cell. This phenomenon is related mainly to the sulfate ion, as electrolytic  $\gamma$ - $\text{MnO}_2$  is most effectively produced in aqueous sulfate-containing media [24].

This work will hopefully be extended to confirm all aspects of the subject, e.g., complete discharge of the cell, recharging, and careful analysis of formed phases. The postulation of possible mechanisms of the reaction that may take place will also be considered.

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