

## Review

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# Preparation and properties of electrolytic manganese dioxide

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### Abstract

A survey has been made of the preparation and properties of electrolytic manganese dioxide, as reported in the literature during the past ten years. This reveals the advantages and disadvantages of using different manganese salts as electrolytes for the preparation of this important depolarizer and the focus of present research investigations.

### Introduction

Manganese dioxide is an essential ingredient in dry cells of the Leclanché type. Because of modern developments in electronic equipment, where weight and volume of the dry cell is fixed while its capacity has to be increased, natural manganese dioxide has been replaced by a synthetic variety, in particular electrolytic manganese dioxide (EMD). Depending on the type of use, this substitution is either partial or total. Production data of this chemical in Japan, which is the major producer of the world, clearly indicate the importance of this chemical, see Table 1. EMD is essential for the fabrication of alkaline cells.

The preparation of EMD from pyrolusite ore involves four major steps: (i) roasting-reduction; (ii) leaching and purification; (iii) electrolysis, and (iv) post-electrolysis. The chemistry involved in these steps can be represented by the following equations:

(i) roasting-reduction:



(ii) leaching:



TABLE 1

Production of electrolytic manganese dioxide (EMD) in Japan

year	1957	1960	1962	1965	1967	1970	1982	1985
EMD (t)	1900	4100	9400	21900	34400	40000	58000	63600

(iii) electrolysis:



Thus, any pure divalent manganese salt on electrolysis between suitable electrodes yields EMD. The nature of the electrolyte influences the physical, chemical and electrochemical properties of the resulting product.

Although sufficient research work has been carried out to understand the process that is involved in each of the above four steps, the electrolysis step attracts the most attention, particularly from the point of view of electrochemistry; it requires further studies.

The present review examines briefly the attempts to prepare EMD from different electrolytes that contain various additives. These studies can be conveniently categorized in terms of the chosen electrolyte system, viz., sulfate, chloride, or nitrate.

### Sulfate electrolyte

The use of a sulfate electrolyte is the conventional method of EMD preparation, as is the case with the electrowinning of metals. The advantages of employing a sulfate electrolyte are:

- (i) a secondary neutralizer, such as lime, can be conveniently employed so that maximum extraction of manganese can be achieved;
- (ii) there are minimal corrosion problems when a lead lining is used;
- (iii) heating of the electrolyte can be carried out using lead coils, and
- (iv) the employment of lead, or its alloys, as electrodes is possible.

The conductivity of sulfate electrolyte is, however, lower than that of chloride or nitrate. The variation of conductivity with concentration has been studied [1].

A variety of anodes has been employed, i.e., lead [2], lead-antimony alloys [3-5], graphite [2, 6], titanium [7-11], platinum [12, 13], RuO<sub>2</sub>-coated titanium [14, 15], MnO<sub>2</sub>-coated titanium [16-19], titanium carbide-coated titanium [20], several types of treated titanium [21, 22], ferrite [23]. The cathodes used have been either carbon [7], lead [8, 10, 17], or titanium [24]. In addition, tubular copper [25] or high surface-area cathodes, such as porous carbon [2], have been employed with a view to reducing the cell voltage and to collecting the hydrogen liberated.

The optimum current density depends on the chosen electrode material, and varies from 50 to 250 A m<sup>-2</sup>. The other operating conditions are MnSO<sub>4</sub>: 0.15 to 2.0 M; H<sub>2</sub>SO<sub>4</sub>: 0.2 to 0.5 M, and temperature: 90 to 97 °C. These conditions provide an average current efficiency of ~90%. The deposit obtained is in the form of a hard compact solid. Detailed studies have been made of the influence of cations or anions that are added to the electrolyte to improve the performance of the depolarizing capability or to assess the dependence of other properties.

### *Influence of cations*

The addition of magnesium sulfate up to a level of 250 g l<sup>-1</sup> has been performed. It has been found that 10 g l<sup>-1</sup> of the salt does not influence the deposition, while excessive amounts cause coarsening of the microstructure of the MnO<sub>2</sub> and the adsorption of microamounts of MgSO<sub>4</sub> in the MnO<sub>2</sub> lattice [7, 12, 26].

The influence of the presence of Fe<sup>2+</sup> at the anode [27] is to decrease the current efficiency due to the formation of the Fe<sup>2+</sup>/Fe<sup>3+</sup> couple. In addition, iron-doped

manganese dioxide behaves differently from ordinary EMD in terms of thermal analysis [28]. The addition of molybdenum (in the form of ammonium molybdate) to  $\text{MnSO}_4\text{-H}_2\text{SO}_4$  electrolyte at a concentration above  $1.6 \times 10^{-4}$  M has been found [24] to inhibit the deposition rate; at  $3.2 \times 10^{-4}$  M the current efficiency is 88% because of the formation of complex species.

It has been shown [7, 29] that the addition of cations such as sodium, ammonium and calcium in trace quantities does not influence the deposition of  $\text{MnO}_2$ . In all cases, the gamma-modification of  $\text{MnO}_2$  is obtained. Doping with vanadium(I) or arsenic has been examined. In case of V(I) doping, the quality of EMD is enhanced as regards the discharge characteristics and the EMD becomes the fibrous gamma-variety [30, 31]. Studies indicate [32] that the inclusion of titanium up to 0.8 wt.% in EMD product (by employing a bath containing either TiS or TiO) improves the discharge performance and especially the rechargeability in alkaline batteries. X-ray diffraction analysis suggests [33] that Ti-doped EMD is  $\gamma\text{-MnO}_2$  with a twisted lattice. EMD is rendered more active, and exhibits a higher recharge capacity, in the presence of silver, Ag(I) [34].

#### *Influence of anions*

The presence of glycine (up to 0.093 M) decreases the current efficiency, both in galvanostatic and potentiostatic studies, by increasing oxygen liberation [35]. The addition of phosphate inhibits the deposition of manganese dioxide; the current efficiency becomes negligible at  $10 \text{ g l}^{-1}$  [6]. The phosphate ion adsorbs on to the anode surface and enhances the rate of oxygen evolution. It has been claimed, however, that small quantities of phosphoric acid or arsenious acid improves the cycle life in alkaline and Li/ $\text{MnO}_2$  batteries [36–38]. Similarly, the presence of selenous acid decreases the deposition rate [39], while that of hydrofluosilicic or acetic or oxalic acid improves the discharge properties of the deposited EMD [40–42]. When poly(vinyl acetate) is added to the electrolyte, in the range of 0.05 to  $1.0 \text{ g l}^{-1}$ , it produces EMD of high surface-area [43]. The addition of nitrate or chloride ion to the sulfate solution modifies the orientation of the growth of EMD as revealed by scanning electron microscopy [44]. The addition of organic additives, such as alcohols, halogenated hydrocarbons, ethers, esters, ketones, aldehydes and carboxylic acids in the bath appears to improve the performance of the Li/ $\text{MnO}_2$  system [45].

#### *Suspension electrolysis*

Though efforts have been made to optimize the conditions to obtain maximum current efficiency, the throughput of the cell is fixed; it depends upon the anode material. Hence, the throughput per cell, especially when a titanium anode is employed, can only be increased by employing suspension electrolysis. In the latter, either oxides of manganese or neutral particles or multivalent insoluble compounds are added to the bath. Because of the modifications employed, it is possible to increase the current density from 100 to  $150 \text{ A m}^{-2}$  and above [46].

With oxides of manganese, the quantity varies from 0.1 to  $10.2 \text{ g l}^{-1}$ ; the particle size is 30 to  $50 \mu\text{m}$  [47–50]. Furthermore, in order to maintain the particles in a suspended state either sparging of air or gases [51–53] or ultrasonic vibration [47, 54] is employed. Gas sparging appears to influence the characteristics of the deposit. For example, the use of oxygen increases the dischargeability of manganese dioxide [53, 55, 56]. Although the quality of the product obtained by a suspension bath has been studied by several authors, and found to be good, commercial adoption of this technique has not yet been made.

Inert particles, such as carbon or titanium nitride, have been added and their influence on the discharge capacity has been examined [54, 57]. It has been found [58] that inclusion of such particles improves the conductivity and, hence, reduces polarization during discharge.

To increase the nonstoichiometry, the addition of multivalent insoluble compounds other than manganese has also been investigated [59].

#### *Simultaneous preparation of EMD and a cathode product*

The theoretical energy required to deposit  $\text{MnO}_2$  at the anode and allow hydrogen to escape at the cathode is: at anode: (+1.23 V  $\times$  26.8 Ah) Wh to obtain 43.45 g  $\text{MnO}_2$ , for 1 kg  $\text{MnO}_2$ : 0.758 kWh, and at cathode: 0 kWh.

But in practice, the energy consumed for deposition is approximately 2.1 kWh per kg with an energy efficiency of  $\sim 40\%$ . As electricity has become more costly, attempts have been made to produce two commercially useful products – one at the anode and another at the cathode. In order to reduce the overall electrical energy consumption, attempts have been on a laboratory scale to achieve simultaneous deposition. The metals deposited have included Zn, Mn, Ni, Fe and Cu. For the winning of Cu, Ni and Mn, suitable diaphragms have been employed. It should be remembered, however, that the optimum conditions for the deposition of  $\text{MnO}_2$  of suitable quality and for that of metals at the cathode vary considerably. Hence, knowledge of engineering design and matching of the quantity of the products have to be employed judiciously.

#### *Mn– $\text{MnO}_2$*

The practicality of combining  $\text{MnO}_2$  deposition with manganese deposition has been studied [60] in a two-compartment cell that employed a porous membrane [61] or PVC-reinforced glass-fibre [62] or anion-exchange membrane [63] as the diaphragm. Attempts have also been made in an undivided cell [64] that contained manganese chloride; this approach is rather surprising. The cathode and anode materials are conventional stainless-steel/Ti and C, respectively, in case of chloride electrolyte, and a stainless-steel cathode and a lead-alloy anode in case of sulfate.

#### *Zn– $\text{MnO}_2$*

Simultaneous deposition of zinc and EMD has been conducted in an undivided electrolytic cell [65–70] that employed aluminium as the cathode [65, 67–70] and either graphite [66] or lead or lead alloy [65, 67–70] as the anode. The composition of the electrolyte was  $\text{MnSO}_4$  (50 to 240 g  $\text{l}^{-1}$ ) and  $\text{ZnSO}_4$  (80 to 300 g  $\text{l}^{-1}$ ) with an acid concentration up to 60 g  $\text{l}^{-1}$ . The temperature of electrolyte was 70 to 90 °C. The current density was varied between 0.7 and 3.0 A  $\text{dm}^{-2}$ . The design was adjusted so that the current density at the cathode was higher than that at the anode. For this cell only 40% of the energy was consumed [69], compared with the total energy consumption of both the products.

#### *Cu/Ni– $\text{MnO}_2$*

The deposition of Cu or Ni [71–74] has been studied in a divided cell with nylon cloth [71]. It has been shown that when EMD is combined with Ni deposition, an overall energy saving of up to 78% could be achieved [74].

#### *EMD as powder*

The hard and compact  $\text{MnO}_2$  deposit that is conventionally obtained at the anode has to be lifted from the cell, stripped from the anode, ground, washed thoroughly

to remove both acid and electrolyte, and then powdered to suitable size. To avoid part of the post-electrolysis treatment, experiments have been carried out to produce powdered manganese dioxide. The advantages claimed are:

- (i) there is no need to lift the anode for the stripping step, and thus decreases the down-time of the electrolytic cell;
- (ii) powdering equipment is not required, and
- (iii) the process can be made continuous and cyclic.

The EMD powder produced at low temperature, high current density and high acid concentration has been found to be of the gamma-variety and to possess a high electrolytic capacity [75].

Fine particles of active manganese dioxide have been prepared by employing a pump cell [76]; the electrolyte was 1 M  $\text{H}_2\text{SO}_4$  and  $\text{MnSO}_4$  at 20 °C. A current efficiency of 86 to 93% has been claimed; the value depends upon the current density. The anode employed was lead coated with lead dioxide. A Ti grid, coated with  $\text{PbO}_2$ , has also been employed for preparation at a current density of 3.5  $\text{A dm}^{-2}$  [77]. The influence of formation on the discharge performance has been studied [78].

The employment of a rotating cylindrical electrode/circulating particulate-bed electrode assembly has been found [79] to be more useful than a conventional stationary anode. An alternative approach is to reverse periodically the polarities of the anode and cathode under suitable electrolytic conditions [80]. These methods of preparation, however, are still to reach commercialization.

### Nitrate electrolyte

Manganese dioxide can also be obtained from nitrate solution. The advantages of employing such a bath are: (i) the solution is highly conductive; (ii) solubility is very high ( $> 1000 \text{ g l}^{-1}$ ) and, (iii) electrical energy consumption is reduced significantly. By contrast, the disadvantages are: (i) high cost; (ii) the nitrate ion reduces at the cathode to form oxides of nitrogen; this makes the process noncyclic unless the oxides of nitrogen are completely converted back to acid.

Research work has been carried out on the deposition of  $\text{MnO}_2$  from a nitrate bath. A high anode current efficiency has been obtained with a very low cell voltage. In addition, the orientation of the growth of EMD differs from that of conventional EMD [81].

### Chloride electrolyte

The next best alternative method to sulfate electrolysis is to prepare EMD from chloride solutions. The advantages are numerous. Because of these, and given the present energy crunch, electrometallurgical processes are being performed in a chloride-medium, e.g., for nickel electrowinning [82]. The benefits include: (i) higher conductivity than the sulfate electrolyte; (ii) utilization of the cheaper by-product, HCl, obtained from the chlor-alkali/PVC industries; (iii) higher solubility of the salt, and (iv) formation of a more active manganese dioxide.

#### *Preparation and properties*

References to chloride electrolytes are few, but careful perusal of the literature reveals the following. An approximate concentration of 1 M  $\text{MnCl}_2$  with 0.35 to 0.75

M HCl has been electrolyzed between a graphite or titanium anode and a graphite cathode to obtain the gamma-form of manganese dioxide [83]. The optimum current density was 10 to 18 A dm<sup>-2</sup>, as determined by the chosen type of anode. Studies have been undertaken [84] on the influence of different operating conditions, such as MnCl<sub>2</sub>/HCl concentration, temperature and current density on the current efficiency, cell voltage, energy consumption, structure (by XRD analysis), activity, MnO<sub>2</sub> content, etc. The temperature of the electrolysis was either 80 or 96 °C. In laboratory-scale experiments with chloride, fibrous electrolytic manganese dioxide (FEMD) was obtained. This is found to be superior in discharge characteristics, because it possesses improved physical properties [85]. The optimum conditions to achieve a current efficiency above 80% are [86]: anodic current density < 2.5 A dm<sup>-2</sup> and HCl 15 g l<sup>-1</sup>. These corroborate the results obtained earlier [84]. The EMD obtained with a higher concentration of HCl, however, exhibits superior electrochemical activity [84, 87]. Physical measurements (e.g., thermoelectric e.m.f.) indicate the existence of n-type semiconductivity [88]. The discharge behaviour of different heat-treated samples has been correlated [89] with the thermoelectric properties. In addition, the discharge behaviour of FEMD has been compared [90] with that of iron-doped manganese dioxide; it was found that the doping of iron increases the discharge efficiency by 8 to 10%, as compared with normal FEMD.

#### *Work performed at the Central Electrochemical Research Institute*

Extensive data have been collected [83] on a pilot-plant (50-kg/day capacity) that employs graphite or titanium anodes in chloride electrolyte. Ores from the Karnataka and Madhya Pradesh regions have been used; these ores are of a medium/high grade. A total of 27 tonnes of ore has been processed. In the pilot plant, a total of 28 tonnes of MnCl<sub>2</sub> have been handled in the form of 10% solution. During these trials, approximately 7 tonnes of EMD has been produced. This has been supplied to various battery industries and has been found to conform to the Japanese standard.

#### **Conclusions**

The following advantages are to be gained by adopting the chloride route in preference to conventional sulfate electrolysis:

- (i) superior quality EMD associated with improved physical, chemical, catalytic and electrochemical properties;
- (ii) consumption of substrate graphite is less, and this leads to a higher purity and longer life of anode;
- (iii) consumption of EMD in the ultimate application is less for the same performance;
- (iv) higher leaching efficiency;
- (v) better working atmosphere due to the absence of sulfuric acid spray;
- (vi) less salt crystallization during electrolysis, and
- (vii) easier washing of the final EMD (due to the absence of entrapped sulfate).

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