

## MANGANESE DIOXIDE -- A REVIEW OF A BATTERY CHEMICAL PART I. CHEMICAL SYNTHESSES AND X-RAY DIFFRACTION STUDIES OF MANGANESE DIOXIDES

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### Summary

This review is concerned with the synthesis of manganese dioxide by chemical methods and by the activation of natural ores. Chemical synthesis usually involves thermal oxidation of Mn(II) (nitrates or carbonates), disproportionation of  $Mn^{3+}$  compounds, oxidation of Mn(II) salt solutions by oxidizing agents such as chlorates, persulphates, ozone, etc, or the reduction of permanganates. The Mn(II) salts are usually obtained by chemical treatment of manganese ores. Low-grade ores require enrichment and separation from materials such as clay, silica, phosphorus, Fe and other undesirable heavy metallic impurities. Electrochemically active manganese dioxides are also obtained by the activation of manganese ores which involves suitable acid treatment of the reduced ores. X-ray diffraction studies of the dioxides indicate different crystalline forms:  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$  and ramsdellite. Of these only  $\beta$ - $MnO_2$  (pyrolusite) and ramsdellite are considered to be true  $MnO_2$  modifications, the other crystalline varieties are apparently non-stoichiometric intergrowth structures of the former and are fundamentally  $\beta$ - $MnO_2$ . This is produced by the cross-linking of the  $MnO_6$  octahedra which formed as a consequence of the hexagonal close-packing of the  $O^{2-}$  ions, with the  $Mn^{4+}$  ions occupying half of the octahedral sites.

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### 1. Introduction

The Zn/ $MnO_2$  "dry" cell has been well developed since its introduction by Leclanché [1] and different versions are available today.

The  $MnO_2$  electrode has been extensively reviewed over the past thirty years or so [2 - 10]. *Batteries Vol 1, Manganese Dioxide*, edited by Kordesch [11], brought together for the first time the developments in both acidic and alkaline Zn/ $MnO_2$  "dry" cells in 1974. The development of primary

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batteries has received further attention from Cahoon and his co-workers [12, 13] and from Tye [14]. Several volumes [15 - 18] are also available covering the investigations of prominent workers in the field. Kozawa [19] has briefly reviewed the properties of  $\text{MnO}_2$  as a typical solid-phase redox system. Takahashi [20] emphasizes  $\text{MnO}_2$  powder technology in the dry battery industry and also discusses the problem concerning carbon for dry cell batteries [21]. Kordesch and Gsellmann briefly reviewed the alkaline  $\text{Zn/MnO}_2$  cell [22]. The manufacture of  $\text{MnO}_2$  has been reviewed by Koshiba [23], Braker [24], Kobayashi and Kozawa [25] and Preisler [26]. Buzowa and Sobolev [27] discussed the structure, specific surface area, water content and electrical conductivity of  $\text{MnO}_2$ . An earlier review of the activation of  $\text{MnO}_2$  for dry batteries was published by Talpade *et al* [28]. Fatiadi [29] gave a great number of references in his review on the use of active  $\text{MnO}_2$  for oxidation in organic chemistry.

The present review is believed to be justified as methods of synthesis, especially non-electrolytic ones, have not been adequately dealt with in any of the above-mentioned works. It is also felt that there is a need for a comprehensive treatment of the solid state and electrochemical aspects of manganese dioxide in view of recent developments in the field.

## 2. Chemical synthesis

Various investigators have synthesized manganese dioxide by different chemical reactions. The  $\gamma\text{-MnO}_2$  crystal phase is the one which has received most attention as it is sought after in the battery industry on account of its very high electrochemical activity. Minor structural variations within the  $\gamma$  phase can lead to wide differences in activity. Various crystallographic forms of  $\text{MnO}_2$ , such as  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  phases, have been synthesized and the same reaction can be employed to obtain any one of these phases by manipulating the reaction conditions. Details of synthesis of the electrochemically active  $\gamma$  crystal phase of  $\text{MnO}_2$  have usually been patented.

Electrolytic methods of synthesizing manganese dioxide are not discussed here as the literature concerned has been extensively reviewed elsewhere [10, 11, 23 - 26]. It is usually prepared [20] by electrolytic oxidation of  $\text{MnSO}_4$  (0.7 - 1.2 mol/l) at about  $90^\circ\text{C}$  with an anode current density of between 0.7 and 1.2  $\text{A/dm}^2$  and either graphite, Pb or  $\text{Tl}$  as the anode material.

### 2.1 Thermal decomposition of Mn(II) nitrates

The synthesis of the well-crystallized stoichiometric  $\beta\text{-MnO}_2$  or "pyrolusite" by thermal decomposition of manganous nitrate is well known [30 - 39]. The method generally involves heating the nitrate in a muffle furnace at about  $180^\circ\text{C}$  for 48 hours. An early worker in the field was Nossen [40] who synthesized  $\text{Mn}(\text{NO}_3)_2$  from a low-grade ore followed by decomposition of the nitrate ( $200 - 300^\circ\text{C}$ ) by the use of heated air and

recycling of the by-products. Subsequently, many workers [41 - 46] employed the above reaction to produce electrochemically active manganese dioxides and there are a number of patents [47 - 50]. Welsh [50] sprayed  $\text{Mn}(\text{NO}_3)_2$  aqueous solutions containing alkaline earth and alkali metal nitrates to form droplets or sheets of solution which partially decomposed to form  $\text{MnO}_2$  and  $\text{NO}_2$ . The solution containing  $\text{MnO}_2$  is recombined with the nitrate solution, sprayed, and fully decomposed to  $\text{MnO}_x$ . Faber [51] reports the formation of  $\gamma\text{-MnO}_2$  by decomposing  $\text{Mn}(\text{NO}_3)_2$  in a current of hot air at 150 - 200 °C.  $\text{MnO}_2$  having a high electrochemical activity is prepared by microwave heating of pure  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [52]. Manganese dioxides doped with foreign cations such as  $\text{Li(I)}$ ,  $\text{Cr(III)}$ ,  $\text{Th(IV)}$ ,  $\text{V(V)}$ , and  $\text{Mo(VI)}$  have also been synthesized [53 - 56] by thermal decomposition of  $\text{Mn(II)}$  nitrate in the presence of small amounts of nitrates of the  $\text{Li}$ ,  $\text{Cr}$  and  $\text{Th}$  cations and vanadates or molybdates for  $\text{V}$  and  $\text{Mo}$ . Valand [57] reported that  $\text{Mo}$ -doped  $\beta\text{-MnO}_2$  in  $\text{Zn}/\text{H}_2\text{SO}_4/\text{MnO}_2$  batteries and  $\text{MnO}_2$ , obtained by heating  $\text{Mn}(\text{NO}_3)_2$  in the presence of a small amount of  $\text{MoO}_3$ , improved the discharge performance of  $\text{Zn}/\text{H}_2\text{SO}_4/\text{MnO}_2$  reserve primary batteries. These batteries are among the ones in which 6 N - 8 N  $\text{H}_2\text{SO}_4$  is used as an electrolyte. The cathode is a lead or lead alloy which is coated with a mixture of  $\text{MnO}_2$ , graphite and carboxymethylcellulose, zinc metal sheet being used as an anode.

## 2.2 Oxidation of manganous hydroxide

Many workers have synthesized manganese dioxide by the oxidation of  $\text{Mn}(\text{OH})_2$  in the presence of air and  $\text{Cl}_2$  [58 - 65]. Wadsley [66] and Buser [67] bubbled air or oxygen through a mixture of manganous hydroxide and sodium hydroxide. This gave intermediate products of uncertain identity which were converted to birnessite or  $\delta\text{-MnO}_2$  by prolonged oxidation. McKenzie [39] recommends bubbling  $\text{O}_2$  for 5 hours through a 2 litre solution at 5 °C containing 0.4 mol  $\text{MnSO}_4$  and 5.5 mol  $\text{KOH}$ . The  $\delta\text{-MnO}_2$  thus obtained is black in colour and contains 9% potassium. It can be transformed to cryptomelane by boiling in a solution containing a limited concentration of  $\text{K}^+$  ions. Beley and Brenet [68] reported the synthesis of a  $\delta\text{-MnO}_2$  having a high catalytic and electrochemical activity after treatment in an acid medium of  $\text{Mn}_3\text{O}_4$ , the latter having been obtained by bubbling of oxygen through  $\text{Mn}(\text{OH})_2$  to oxidize it. Active  $\text{MnO}_2$  has been prepared by other workers [69, 70] following a similar method of oxidation of manganous hydroxide.  $\text{MnO}_2$  of high electrochemical activity was also obtained by passing oxygen under pressure (0.5 MP) through a 200 ml solution of 0.2 manganous acetate at 220 °C for 3 - 6 hours, followed by rapid cooling [71]. Shiramoto [72] synthesized active  $\text{MnO}_2$  by mixing 300 ml of 1 M aqueous  $\text{MnSO}_4$  with 300 ml of 8%  $\text{NaOCl}$ .

## 2.3 Disproportionation of $\text{Mn(III)}$ compounds and oxidation with ozone

Manganite ( $\gamma\text{-MnOOH}$ ) is known to undergo a disproportionation reaction in  $\text{HNO}_3$  leading to the formation of  $\gamma\text{-MnO}_2$  [73].  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$

also undergo disproportionation reactions in the presence of  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ , usually, leading to  $\gamma\text{-MnO}_2$ .

This reaction has been investigated in detail by Brenet and co-workers [74 - 85]. Purol [86] reports studies on the kinetics of the disproportionation of  $\text{Mn}_2\text{O}_3$  in sulphuric acid.  $\alpha$  and  $\gamma$  forms of  $\text{MnO}_2$  are obtained by the reaction of  $\text{Mn}_2\text{O}_3$  with dilute or moderately concentrated acids such as  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  or  $\text{HOAc-HNO}_3$  mixtures and also in the presence of various cations [51, 87, 88]. A  $\delta\text{-MnO}_2$  having an electrochemical activity as high as  $\gamma\text{-MnO}_2$  is obtained by the treatment of  $\text{Mn}_3\text{O}_4$  with excess of 2.33 M  $\text{H}_2\text{SO}_4$  at 25 °C [89]. Giovanoli and co-workers [90 - 92] obtained  $\gamma\text{-MnO}_2$  by disproportionation of  $\text{Mn}_3\text{O}_4$  in excess of  $\text{HNO}_3$ . They observed that prolonged standing or boiling of the  $\gamma\text{-MnO}_2$  in excess acid leads to crystallization and subsequent nucleation to  $\beta\text{-MnO}_2$  [92]. With little acid, the solid product of the reaction of  $\text{Mn}_3\text{O}_4$  with  $\text{HNO}_3$  is  $\gamma\text{-MnOOH}$ . Ramsdellite is reported to have been synthesized by the oxidation of natural or synthetic groutite, *i.e.*  $\alpha\text{-MnOOH}$  [93, 94].

Faber *et al* [95] produced  $\gamma\text{-MnO}_2$  of high electrochemical activity by adding  $\text{HClO}_4$  (20%, 40 °C) to  $\text{Mn}_2\text{O}_3$ , followed by heating for 1 hour at 90 °C. They have also synthesized an active  $\text{MnO}_2$  by the treatment of a finely divided manganous salt with an  $\text{HClO}_4\text{-HNO}_3$  mixture followed by heating between 150 and 250 °C [96]. Faber and Brenet [51, 95] produced a highly active  $\gamma\text{-MnO}_2$  by oxidation of manganous perchlorate (20%) with ozone at 50 °C. The process can be modified to get  $\alpha\text{-MnO}_2$  by adding cations (0.5% - 5%) such as  $\text{K}^+$ ,  $\text{Ca}^{2+}$  or  $\text{NH}_4^+$ , whose radii are larger than that of  $\text{Mn}^{4+}$ , to the solution.

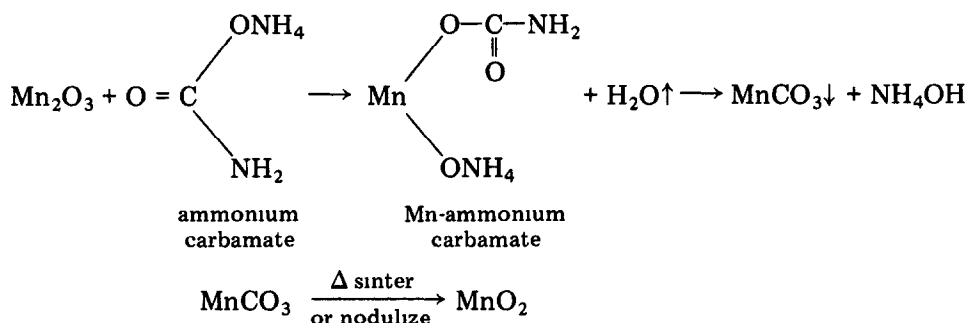
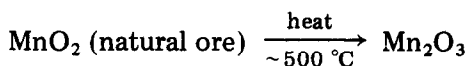
#### 2.4 Manganous carbonate

Many workers have synthesized highly active  $\text{MnO}_2$  by air oxidation of  $\text{MnCO}_3$ , usually in the temperature range 260 - 280 °C [97 - 103]. Most of these methods are patented.  $\text{MnO}$  obtained by thermal decomposition of  $\text{MnCO}_3$  has to be oxidized to  $\text{MnO}_2$  by using 10% sodium hypochlorite solution in the pH range 4 - 5 [104]. Manganese dioxide having a large surface area, and useful as a catalyst, is made by reacting an aqueous  $\text{MnCO}_3$  suspension with  $\text{NaOCl}$  as oxidizing agent [105].  $\text{MnO}_2$  of high activity was also obtained by thermal decomposition of  $\text{MnCO}_3$  in air at a pressure of 5 atm (0.5 MP) [106].

A unique  $\text{MnO}_2$  is Sedema's Faradiser "M" ( $\text{MnO}_2$ , 90.45%, "tap density"\*<sup>2</sup>, 1.63 g/cm<sup>3</sup>), obtained by thermal oxidation of a dense  $\text{MnCO}_3$ , which is obtained by the decomposition of manganese ammonium carbamate. The carbamate was first prepared by leaching reduced ore with ammonium carbamate (the "Dean process") [107]. The reactions involved may be summarized as follows [108]:

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\*"Tap density", is defined as the apparent density of a powder loosely compacted in a graduated cylinder before the volume is determined



The Faradiser "M" is claimed to be suitable for light load, low voltage cells. Recent reports [107a], however, also indicate that Faradiser "M" is suitable even for heavy drain applications — so much so that the present quality of Faradiser "M" seems to offer a reliable alternative to electrolytic manganese dioxide (EMD). In the U S it is used exclusively for Mg/MnO<sub>2</sub> cells [108]. Welsh [109] has similarly obtained MnCO<sub>3</sub> by leaching MnSO<sub>4</sub> with ammonium carbamate between 65 and 68 °C to maintain the oxidizability to MnCO<sub>3</sub>. The carbonate obtained is oxidized to crude MnO<sub>2</sub> in air. The MnO<sub>2</sub> is further enriched by the use of sodium chlorate in acid medium.

Tanabe [110] synthesized catalytic manganese dioxide (CMD) (I C 5) by the oxidation of MnCO<sub>3</sub> at 300 °C. This MnO<sub>2</sub> is not desirable in a battery owing to its comparatively low density (1.23 g/cm<sup>3</sup>) which is attributed to the use of low density MnCO<sub>3</sub>. The latter was synthesized by adding drops of Na<sub>2</sub>CO<sub>3</sub> to MnSO<sub>4</sub> at about 80 °C and stirring for 60 - 90 min. Tanabe *et al* [111, 112] also reported obtaining an improved MnO<sub>2</sub> by initially synthesizing a dense MnCO<sub>3</sub>. A natural ore was reduced to MnO by heating. The MnO was then converted to the manganese ammonium carbamate which, when heated to 79 °C, produced the densest MnCO<sub>3</sub>. The latter was oxidized to crude MnO<sub>2</sub> either by treatment with 50% wet O<sub>2</sub> at normal pressure and at 300 °C for 10 hours to give 85.6% MnO<sub>2</sub> of "tap" density 1.76 g/cm<sup>3</sup>, or by treatment with 50% wet air at normal pressure and at 300 °C for 6 hours for a 77.8% MnO<sub>2</sub> of "tap" density 1.76 g/cm<sup>3</sup>. The crude MnO<sub>2</sub> was then enriched by reacting it with NaClO<sub>3</sub> in the presence of a small excess of H<sub>2</sub>SO<sub>4</sub> and with added MnCO<sub>3</sub>. After 1 hour at 95 °C enriched MnO<sub>2</sub> (91.4%, "tap" density 2.31 g/cm<sup>3</sup>) was obtained. The product was found to be suitable for intermittent light discharge. It is also believed that with a proper choice of electrolytic solution and cathode mix the product could be used at a higher discharge rate with a much improved intermittent discharge performance [112].

## 2.5 Oxidizing agents such as chlorates, bromates and persulphates

Active manganese dioxides can be synthesized by the oxidation of manganous salts using oxidizing agents such as sodium chlorate or bromate and ammonium perchlorate or persulphate [85, 113 - 116]. Giovanoli *et al* [117] synthesized crystals of  $\gamma$ - $\text{MnO}_2$  by oxidizing  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (100 g in 4 L  $\text{H}_2\text{O}$  with 0.2 L 2 N  $\text{HNO}_3$ , heated to between 55 and 85 °C) by the slow addition of 225 g ammonium persulphate. Crystallite growth is enhanced by heating the initially needle-like crystals in 2 N  $\text{HNO}_3$  under reflux.

Julian [118] was one of the first to suggest that manganese dioxide could be obtained by oxidation of manganese salts. The reaction was usually carried out in a strong  $\text{HNO}_3$  medium and at temperatures between 60 and 80 °C. Gruner [119] obtained an amorphous  $\text{MnO}_2$  by the addition of  $\text{KClO}_3$  to pure  $\text{Mn}(\text{NO}_3)_2$  in nitric acid. On repeating the above experiment, however, he found that a pyrolusite was formed in place of the amorphous material. Gruner, therefore, expressed the view that there was no way of predicting which oxide the above reaction would produce. Cole *et al* [120], however, were able to obtain pure cryptomelane ( $\alpha$ - $\text{MnO}_2$ ) by the same method as used by Gruner, *viz* by the action of  $\text{HNO}_3$  and  $\text{KClO}_3$  on  $\text{MnSO}_4$  and by heating the resulting amorphous substance at 400 °C. Welsh [113] prepared  $\text{MnO}_2$  of high electrochemical activity by chlorate oxidation and has patented the technique. Various combinations of catalytically active manganese dioxides and chlorate oxidized manganese dioxides have been found to give exceptionally good battery performance [121]. Recently, Desai [122] determined the optimum conditions necessary for complete oxidation of manganous salts by potassium chlorate. Brooks [123] has reported the synthesis of a  $\gamma$ - $\text{MnO}_2$  having high electrochemical activity by  $\text{NaClO}_3$  oxidation of  $\text{Mn}(\text{NO}_3)_2$  in  $\text{HNO}_3$ .

The  $\text{KClO}_3$  oxidation of  $\text{Mn}(\text{NO}_3)_2$  in a solution of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  has been studied by Kanoh *et al* [124, 125] who suggested a mechanism for the reaction. In an  $\text{HNO}_3$  solution the reaction is controlled by conditions that accelerate the oxidizing action of  $\text{ClO}_3^-$  and a  $\gamma$  phase is obtained. In a solution containing  $\text{H}_2\text{SO}_4$ , the reaction rate is determined by the disproportionation of  $\text{Mn}^{3+}$  and  $\alpha$ - $\text{MnO}_2$  containing 6% K in its crystal structure is obtained. Both  $\gamma$ - and  $\alpha$ - $\text{MnO}_2$  are found to show relatively good discharge performance in neutral solutions. Recently, Fernandes *et al* [126] reported detailed investigations of the chlorate reaction which is involved in the synthesis of manganese dioxides by  $\text{KClO}_3$  and  $\text{NaClO}_3$  oxidation of both  $\text{MnCl}_2$  and  $\text{MnSO}_4$  in concentrated  $\text{HNO}_3$  at 100 °C. In all cases  $\alpha$ - $\text{MnO}_2$  was obtained when  $\text{MnSO}_4$  was used. With  $\text{MnCl}_2$ , a  $\gamma$  phase was obtained only when  $\text{KClO}_3$  was added in small amounts. A mixed ( $\alpha$ ,  $\gamma$ ) crystal phase was obtained when only one lot of the required  $\text{KClO}_3$  was added. A  $\gamma$  phase is preferably obtained with  $\text{NaClO}_3$ . The  $\alpha$  and ( $\alpha$ ,  $\gamma$ ) mixed crystal phase types exhibit exceptionally high catalytic activity. The  $\gamma$ - $\text{MnO}_2$  samples show excellent discharge performance in 9 M KOH solutions [127]. Welsh [128] reports the synthesis of a special  $\text{MnO}_2$  for batteries by  $\text{NaClO}_3$  oxidation of  $\text{MnSO}_4 \cdot \text{MnO}_2$  with improved dis-

charge performance was also obtained by heating a 50% aqueous NaOH solution in an autoclave at 180 °C and at 5 atm (0.5 MP) [129].

## 2.6 Reduction of permanganates

$\gamma$ -MnO<sub>2</sub> has been synthesized by reducing permanganates in a boiling MnSO<sub>4</sub> solution [116, 130, 131]. Catalytically active MnO<sub>2</sub> has been made by reducing alkaline KMnO<sub>4</sub> with MnSO<sub>4</sub> [132]. Certain gel forms of MnO<sub>2</sub> are formed by the controlled reduction of acidified NaMnO<sub>4</sub> and KMnO<sub>4</sub> with MnOS<sub>4</sub> solution [116].  $\alpha$ -MnO<sub>2</sub> is obtained by the decomposition of permanganic acid solution or by the action of H<sub>2</sub>O<sub>2</sub> on KMnO<sub>4</sub> or by adding dilute MnSO<sub>4</sub> to a dilute KMnO<sub>4</sub> solution [133]. The addition of HCl to boiling KMnO<sub>4</sub> solution also gives  $\alpha$ -MnO<sub>2</sub> [134] and it is reported that a brown precipitate of K<sup>+</sup> containing  $\alpha$ -MnO<sub>2</sub>, and having excellent discharge capacity, is synthesized by the addition of 6 N HCl to a 0.1 M boiling KMnO<sub>4</sub> solution [135]. Berg *et al* [136] have synthesized active MnO<sub>2</sub> by spraying permanganic acid over a heated (150 - 200 °C) granite slab.  $\delta$ -MnO<sub>2</sub> is produced by the reduction of KMnO<sub>4</sub> with hydrochloric acid [137] or with H<sub>2</sub>O<sub>2</sub> [138], and Maxwell and Thirsk [139] obtained  $\delta$  and  $\alpha$  forms of MnO<sub>2</sub> by adding drops of HCl to boiling permanganates of K, Ca and Ba. McKenzie [39] has reported the synthesis of a brown birnessite ( $\delta$ -MnO<sub>2</sub>) with a potassium content of 9.5% by adding drops of two moles of concentrated HCl to a boiling solution of 1 mole of KMnO<sub>4</sub> in 2.5 litres of water. The formation of active MnO<sub>2</sub> by the reduction of permanganate with sodium tetrahydroborate in a weak alkaline medium has also been reported [140].

The synthetic Mn(IV) oxide prepared by reducing KMnO<sub>4</sub> in an alkaline solution is usually hydrous MnO<sub>2</sub> containing large amounts of chemically bound water [141]. Hydrous MnO<sub>2</sub> suitable for use in batteries is obtained as a by-product in several chemical industries (the manufacture of saccharine, vitamins, etc.) where KMnO<sub>4</sub> is used as an oxidizing agent [142, 143]. Narita and Okabe [144] synthesized hydrous MnO<sub>2</sub> by reducing alkaline KMnO<sub>4</sub> with H<sub>2</sub>O<sub>2</sub>, K<sub>2</sub>SO<sub>3</sub>, and KNO<sub>2</sub> as well as by disproportionation of K<sub>2</sub>MnO<sub>4</sub> solution. Mehta and Baxi [145] synthesized hard granular hydrous manganese dioxide having good ion-exchange properties by reduction of KMnO<sub>4</sub> with KI or MnSO<sub>4</sub> in an alkaline medium.

Hunter [146] reported the synthesis of a new crystal form of  $\lambda$ -MnO<sub>2</sub> by the treatment of LiMn<sub>2</sub>O<sub>4</sub>, a spinel-type material, with an aqueous acid. It has a structure related to the spinel, with most of the Li removed from the tetrahedral sites. The conversion is accompanied by lattice contraction. According to a Japanese patent (*Jpn Appl*, 55-100224, (31 Jul. 1980)), LiMn<sub>2</sub>O<sub>4</sub> having a spinel structure can be made by heating a mixture of Li<sub>2</sub>CO<sub>3</sub> and MnO<sub>2</sub> (in a ratio Mn:Li = 2:1) at 800 - 900 °C. The  $\lambda$ -MnO<sub>2</sub> was reported to exhibit a discharge performance superior to a heat-treated EMD. Miyake [147] explained and summarized the procedures for interconversions among various MnO<sub>2</sub> polymorphs ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ) with relevant references.

## 2 7 Summary of chemical synthesis

Faradiser "M" is considered to be the best chemical manganese dioxide which can compete with electrolytic manganese dioxide in the battery industry.

There seems to be plenty of scope, however, for synthesizing chemical manganese dioxides by employing various chemical reactions, taking into consideration the following crucial factors:

- (i) economics of the process,
- (ii) synthesis of the  $\gamma$  crystal phase,
- (iii) high "tap" density.

The methods with which to obtain the dioxides that satisfy the above criteria are usually patented.

## 3. Enrichment and leaching of manganese ores

The leaching of  $MnO_2$  ores is usually concerned with the conversion of the dioxides to Mn(II) salts such as  $MnSO_4$ ,  $MnCl_2$ ,  $MnCO_3$ ,  $Mn(NO_3)_2$  by suitable chemical treatment. Since a crude ore contains inclusions such as clay and other minerals, it is purified by flotation, washing, magnetic separation, etc., before being converted into Mn(II) salts. The salts are further purified to remove undesirable metallic impurities such as Fe, Al, Co, Ni, Cu, etc., usually by a series of pH adjustments [148]. The content of heavy metals which can be tolerated in dioxides for batteries is roughly as follows [108]. As, Sb, Mo, Sn, Ni, Co, Cu, Ge, etc., less than 0.001%, and Fe less than 1%.

### 3 1 Enrichment of low-grade manganese ores

Low-grade ores can be enriched by foam separation, polygradient magnetic separation, gravity separation, reversed flotation, selective flocculation techniques, etc. [149 - 157] to remove impurities such as  $CaO$ ,  $SiO_2$ , P and other. The removal of alkali metal and alkaline earth impurities has also been reported [158].  $SiO_2$  and  $Al_2O_3$  can be removed from Mn ores by heating the ores with alkali, followed by additions of small amounts of powdered lime, and allowing the suspensions to equilibrate for 2 days at room temperature [159]. Lean manganese ores and limes have been enriched by various workers [160 - 164] with nitric acid,  $SO_2$  and  $H_2SO_4$ . Kanungo and Sant [165, 166] reported the dephosphorization of the phosphorus-rich manganese ores of Central India (ground 100 mesh particles) by selective leaching between 30 and 70 °C for 2 hours in dilute mineral acids ( $HCl$ ,  $HNO_3$ ,  $H_2SO_4$ ). Seventy to ninety percent of the phosphorus was removed and all acids were found to be equally effective. Some ore samples only responded to treatment to remove the phosphorus after being heated to between 700 and 900 °C. It has also been reported in an Indian patent [167] that the phosphorus content in manganese oxide ores could be reduced by heating the ore with  $Na_2CO_3$  and water at 200 °C



for 30 min and at 800 °C for 90 min, followed by repeated leaching in boiling water. Phosphorus removal was also achieved by heating the ore with NaSO<sub>4</sub> for 1 hour at 950 °C and leaching it for 30 min at 80 °C with a solid:liquid ratio of 1:3 [168]. Several studies of phosphorus removal techniques have been reported [169 - 177], but details are not available. Recently, Fomin [176] reviewed the enrichment and dephosphorization of manganese ores in the Nikopol and Chatura Basins.

### 3 2 Preparation of Mn(II) salts for synthesis of manganese dioxides

Manganous sulphate is usually prepared by leaching the ores with sulphuric acid [178 - 183]. The powdered ore is heated with H<sub>2</sub>SO<sub>4</sub> at 900 °C for 30 min, cured for 48 hours, dried in a muffle furnace at 550 °C for 8 hours, cooled and leached with water and, finally, filtered. Most of the Fe is removed by treatment with Na<sub>2</sub>CO<sub>3</sub> and the filtrate is recrystallized to obtain MnSO<sub>4</sub> [178, 123]. Almassy *et al* [179] leached the ore with concentrated H<sub>2</sub>SO<sub>4</sub>, then treated the salt with NaOH and used air for oxidation to obtain MnO<sub>2</sub> of good electrochemical activity. Manilici *et al* [181] reduced a low-grade Mn ore with dissociated ammonia or methane at 900 °C, followed by leaching with H<sub>2</sub>SO<sub>4</sub> at 40 °C. Demurya and Agladze [183] leached their ore with aqueous H<sub>2</sub>SO<sub>4</sub>, precipitated Fe and Al from the solution, and electrolysed the resulting solution. Factors affecting the sulphuric acid leaching efficiency have also been studied [184 - 186]. Ore which has been pre-reduced at 1000 °C with pure graphite powder has been shown to leach better [186]. MnSO<sub>4</sub> can also be obtained by treating the ores with SO<sub>2</sub> gas in H<sub>2</sub>SO<sub>4</sub> and other sulphate compounds [187 - 195]. Yousef and co-workers [189] reported the enrichment of a low-grade Mn ore by suspending the pulverized ore in water at 40 °C through which was passed an SO<sub>2</sub>-NO mixture. It was then leached with water in a CO<sub>2</sub>-air mixture. The Mn(II) salt obtained was oxidized with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to obtain γ-MnO<sub>2</sub> of high electrochemical activity.

Some workers [148, 196, 197] used (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> for leaching the ores to produce MnSO<sub>4</sub>. Pigão and Pesigan [148] roasted a 200 mesh low-grade ore with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at 500 °C for 2 hours. The MnSO<sub>4</sub> obtained was leached with water and Fe, P and SiO<sub>2</sub> were removed by a series of pH adjustments. The use of FeSO<sub>4</sub> for leaching ores has also been reported [198, 199]. Astoff [198] produced MnSO<sub>4</sub> by digesting an ore (MnO<sub>2</sub>, 38.5%; Fe<sub>2</sub>O<sub>3</sub>, 20.8%, SiO<sub>2</sub> 26.9%, Al<sub>2</sub>O<sub>3</sub> 6.5%) with aqueous FeSO<sub>4</sub> for 30 min at 90 °C. The MnSO<sub>4</sub> was then separated from the insoluble Fe(OH)<sub>3</sub> by filtration and MnSO<sub>4</sub>·H<sub>2</sub>O was obtained by crystallization of the filtrate. Das and co-workers [199] investigated the optimum conditions for FeSO<sub>4</sub> leaching of the low-grade ores of Orissa, India. The effect of acid additions during FeSO<sub>4</sub> leaching of the ore was determined. They also reported [200] the production of MnSO<sub>4</sub> from ferromanganese slag (28% Mn) and from a low-grade ore (40% Mn). Leaching by agents such as diluted H<sub>2</sub>SO<sub>4</sub>, FeSO<sub>4</sub>, FeSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> mixtures or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-FeSO<sub>4</sub> mixtures was followed by electrolysis of the MnSO<sub>4</sub> solution to give γ-MnO<sub>2</sub>. Some workers have also reported

the production of potassium manganates from ores [201, 202]. Tanabe *et al* [203] describe the production of  $\text{MnCO}_3$  by the treatment of pyrolusite with  $\text{CO}_2$  in a patent, but there is no evidence that it works. After removing impurities such as Fe, Al, Co, Ni, Cu, etc. by treating the  $\text{MnCO}_3$  with  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$ , the purified  $\text{MnCO}_3$  was decomposed to  $\text{MnO}_2$  of high electrochemical activity.

$\text{MnCl}_2$  is usually prepared by leaching the ore with concentrated hydrochloric acid [178, 204, 205]. Swinkels *et al* [204] then treated the  $\text{MnCl}_2$  with  $\text{Cl}_2$  (evolved in the leaching step) to precipitate impurities, while precipitating  $\text{MnO}_2$  by maintaining the pH at 0.5 with the addition of a base. Carbon black was added during the  $\text{MnO}_2$  precipitation to improve the performance of the product in batteries. The factors affecting the efficiency of the leaching of a low-grade ferruginous Mn ore with concentrated HCl were also discussed [206]. Manganous nitrate can be obtained by leaching the reduced ore with nitric acid [178, 207].  $\text{MnO}_2$  of high electrochemical activity was produced by the thermal decomposition of  $\text{Mn}(\text{NO}_3)_2$  prepared by leaching the ores with nitrous or nitric acids [208 - 213]. The salient feature of the Welsh process is leaching of  $\text{MnO}_2$  ore slurry by a parallel stream of gaseous nitrous oxides, thus avoiding the formation of  $\text{HNO}_3$  as  $\text{NO}_2$  gets oxidized with excess  $\text{MnO}_2$ . The other characteristic feature is the decomposition of  $\text{Mn}(\text{NO}_3)_2 \cdot m\text{H}_2\text{O}$  melt by heating the melt under vigorous agitation. This prevents the scaling of  $\text{MnO}_2$  on the walls of the vessel.

#### 4. Activation of manganese ores

Most of the natural  $\text{MnO}_2$  ore deposits are inactive and require activation treatment before being used as active cathode materials in dry cells. A number of workers [214 - 216] introduced different methods for the activation of ores. It is usually carried out by the disproportionation method [75, 217, 218] which involves the reduction of  $\text{MnO}_2$  to  $\text{Mn}_2\text{O}_3$  by heat treatment, sometimes in the presence of a reducing agent such as graphite or carbon black.  $\text{Mn}_2\text{O}_3$ , on treatment with dilute mineral acids such as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  etc., undergoes a disproportionation reaction to yield electrochemically active  $\text{MnO}_2$  and Mn(II) salt in the corresponding acid. The factors affecting the efficiency of the disproportionation process and the nature of the  $\text{MnO}_2$  product obtained have also been determined [219]. The disproportionation process is known to be a reversible one [220], and therefore the acid treatment is one of the key factors which determines the nature and yield of the final product. In general, it has been found [218 - 223] that insufficient quantity of  $\text{H}_2\text{SO}_4$  favours the formation of  $\text{MnOOH}$ , while hot concentrated  $\text{H}_2\text{SO}_4$  tends to produce  $\text{Mn}_2(\text{SO}_4)_3$ .

Many workers [224 - 232] have reported the synthesis of electrochemically active manganese dioxides by the activation treatment. Most of these are patents. Rosetti [226] reported the synthesis of  $\text{MnO}_2$  of high

electrochemical activity by roasting pyrolusite in the presence of carbon, quenching the hot reduced mass in water, then treating it with an acid such as 10%  $\text{H}_2\text{SO}_4$ . The treatment of finely divided ore with 15%  $\text{H}_2\text{SO}_4$  at 50 - 60 °C followed by washing with soft water and drying, also produces active  $\text{MnO}_2$  [229], as does the roasting of pyrolusite at 600 °C, followed by acid leaching [230]. Takahashi *et al* [233, 234] studied the activation treatment and reported the optimum conditions for activation [109]. They crushed inactive  $\text{MnO}_2$  ore to less than 100 mesh, heated it for 4 hours at 700 °C and then leached it in 1 litre of hot dilute  $\text{H}_2\text{SO}_4$  (1:9) at 90 °C for 30 min. The activated ore was neutralized in a 5% aqueous solution of bicarbonate (containing 2% of  $\text{NH}_4\text{Cl}$  as a peptization inhibitor), washed in hot water, and dried at 70 - 80 °C (yielding 55.6%).

Utani *et al* [235] roasted an African ore at 650 - 750 °C in a rotary kiln to get  $\text{Mn}_2\text{O}_3$  which was leached in hot dilute  $\text{H}_2\text{SO}_4$  to obtain active  $\text{MnO}_2$ . The product (AMD) was tested in a practical  $\text{ZnCl}_2$  cell. Its efficiency was found to be equal to that of I.C.1 (EMD) on intermittent discharge and was higher than that of EMD on 2 and 10  $\Omega$  continuous discharge. Nevertheless, these results do appear to be surprising. The discharge duration of the AMD, however, was 60% - 80% of that of an EMD cell because of its low packing density. Komiyama [236] also reported synthesis of an activated  $\text{MnO}_2$  by a similar procedure. He found that its overall discharge performance was close to that of EMD in  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$  batteries.

## 5. X-ray diffraction studies

There is abundant literature on the characterization of the manganese dioxides by the X-ray powder diffraction technique (Table 1). It involves the identification and location of manganese, oxygen and hydroxyl ions in the unit cells. A detailed bibliography is readily available in two papers by Burns *et al* [237, 238] and in some of the reviews cited earlier [5 - 10], as well as in the work of Ettel and Veprek-Siska [239]. This will not, therefore, be reproduced here.

### 5.1 General structural features

Fleischer and Richmond [240], Brenet and Héraud [241] and Cole *et al* [120] used X-ray powder diffraction to characterize a large number of manganese dioxides obtained by various methods, and the crystal phases such as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$  and their subtypes were identified. Most of the ambiguities involved in the nomenclature have been resolved and classified by Tauber [242]. Nye *et al* [243] were probably amongst the first to provide a basis for describing the crystal structure of the dioxides by tracing their genesis to  $\text{Mn-O}\cdot\text{OH}$  type compounds on the basis of a compositional diagram of the manganese-oxygen-hydroxyl system. The structures are believed to involve hexagonal close packing of the oxygen and hydroxyl

TABLE 1

Typical X-ray powder diffraction data for  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -manganese dioxides

$\alpha$ -MnO <sub>2</sub> [255] Tetragonal			$\beta$ -MnO <sub>2</sub> [255] Tetragonal			Chemical $\gamma$ -MnO <sub>2</sub> [249] Orthorhombic	$\gamma$ -MnO <sub>2</sub> (ASTM 14-644) Orthorhombic		
<i>hkl</i>	<i>d</i>	<i>I/I</i> <sub>0</sub>	<i>hkl</i>	<i>d</i>	<i>I/I</i> <sub>0</sub>	<i>d</i>	<i>hkl</i>	<i>d</i>	<i>I/I</i> <sub>0</sub>
110	6 938	s	110	3 084	w	3 930	110	3 96	100
200	4 901	vs				2 624	130	2 60 <sup>+</sup>	60
220	3 467	vvw	101	2 393	s	2 430	021	2 42	140
310	3 109	vvs				2 346	111		
			200	2 189	vvw				
410	2 393	vvs				2 328	040	2 32 <sup>+</sup>	80
			211	1 623	s				
301	2 148	s				2 225	200		
			220	1 557	w				
510	1 928	uvw				2 133	121	2 12	80
			002	1 435	w	2 064	140	2 05 <sup>+</sup>	40
411	1 830	s	310	1 398	vvw	1 863	131		
511	1 633	w(br)	301 } 112 }	1 306	s	1 642	221	1 637	80
540	1 537	w				1 609	240	1 605 <sup>+</sup>	60
601	1 427	w				1 497	151	1 486 <sup>+</sup>	10
			202	1 204	vvw	1 426	002	1 422 <sup>+</sup>	60
							161		
						1 361	061	1 320 <sup>+</sup>	40
<i>a</i> = 9 81 Å <i>c</i> = 2 853 Å			<i>a</i> = 4 428 Å <i>b</i> = 2 878 Å			<i>a</i> = 4 45 Å <i>b</i> = 9 305 Å <i>c</i> = 2 85 Å			

s = sharp, v = very, w = weak, br = broad

<sup>+</sup>In electrolytic MnO<sub>2</sub>, the lines marked <sup>+</sup> are missing

ions with half of the octahedral sites occupied by Mn<sup>4+</sup> and some Mn<sup>3+</sup> ions. Consequently, octahedra form in which the Mn<sup>4+</sup> ion is surrounded by six O<sup>2-</sup> ligands with an average Mn-O distance of 1.88 Å [238]. The hydroxides tend to form sheets of edge-sharing co-ordination octahedra and the oxides tend to form chains of edge-sharing octahedra [243]. Reasons for hexagonal close-packed oxygen and the straight chains are not very clear and MnO<sub>2</sub> could, conceivably, exist also with cubic close-packed layers as well as kinked chains of octahedra [244]. It is doubtful whether the X-ray diffraction pattern of fine MnO<sub>2</sub> powder could be used to detect such structures if they were present, for example, locally in "active" MnO<sub>2</sub>. Further, a careful look at the X-ray data of the MnO<sub>2</sub> phase reveals that the lines at 2.40 Å and 1.42 Å are present in most of the phases as well

Electrolytic MnO <sub>2</sub> [291] Orthorhombic		$\gamma$ -MnO <sub>2</sub> , chlorate method [255] Orthorhombic			Hexagonal	$\delta$ -MnO <sub>2</sub> [255] Hexagonal		
<i>d</i>	<i>I/I</i> <sub>0</sub>	<i>d</i>	<i>I/I</i> <sub>0</sub>	<i>hkl</i>	<i>hkl</i>	<i>d</i>	<i>I/I</i> <sub>0</sub>	
4 10	100	4 075	w(br)	101	10 $\bar{7}$ 0	7 183	w(br)	
2 43	100	2 405	w	301	11 $\bar{0}$ 0	3 006	vvw	
					20 $\bar{0}$ 1	2 553	vvw	
					2 $\bar{0}$ 02	2 429	s	
		2 112	s	400	21 $\bar{3}$ 1	2 169	vvw	
2 13	80	1 627	s	330	22 $\bar{0}$ 1	1 496	vvw	
1 64	80				31 $\bar{0}$ 2	1 411	w(br)	
1 40	60	1 389	w	340				
		<i>a</i> = 4 432 Å		<i>a</i> = 9 75 Å	<i>a</i> = <i>b</i> = 6 022 Å			
		<i>b</i> = 10 75 Å		<i>b</i> = 9 75 Å	<i>c</i> = 12 505 Å			
		<i>c</i> = 2 706 Å		<i>c</i> = 4 628 Å				

as in naturally occurring minerals having the same phase. These lines are representative of diffraction from atomic planes of hexagonal close-packed oxygen containing Mn<sup>4+</sup> ions in octahedral co-ordination with oxygen, in which the [MnO<sub>6</sub>] octahedra share edges. The 2.40 Å and 1.42 Å spacings, therefore, correspond to the (10 $\bar{1}$ 0) and (1 $\bar{1}$ 20) planes of the hexagonal close-packed system [245]. The Mn-Mn intermetallic distance across the shared octahedra is 2.84 - 2.88 Å, and this dimension (or multiples of it) commonly appears in the cell parameters of Mn(IV) oxides.

### 5.2 Pyrolusite/ramsdellite the true MnO<sub>2</sub> modifications

The fundamental structure for describing the crystal forms of the various crystalline phases is that of pyrolusite or  $\beta$ -MnO<sub>2</sub> [238] (Fig. 1). The [MnO<sub>6</sub>] octahedra share edges to form single chains extending along

the *c*-axis with Mn–Mn internuclear distance, 2.87 Å, as a common cell parameter. The chains are cross-linked with neighbouring chains by the corner sharing of oxygen atoms of adjacent octahedra. The  $\beta$ -MnO<sub>2</sub> is described as a rutile structure [246, 247], but the ideal rutile structure is never met; the [MnO<sub>6</sub>] octahedra are distorted in such a way that the three coplanar 120° Mn<sup>4+</sup>–O bonds are preferred to the single 90° and the two 135° angles which would exist if all octahedra were regular [243, 244, 248]. The net result appears to be a lattice expansion in the *c*-direction and a contraction in the other two. For each MnO<sub>2</sub> there are four empty tetrahedral sites, half of them sharing two faces with two Mn<sup>4+</sup> octahedra and

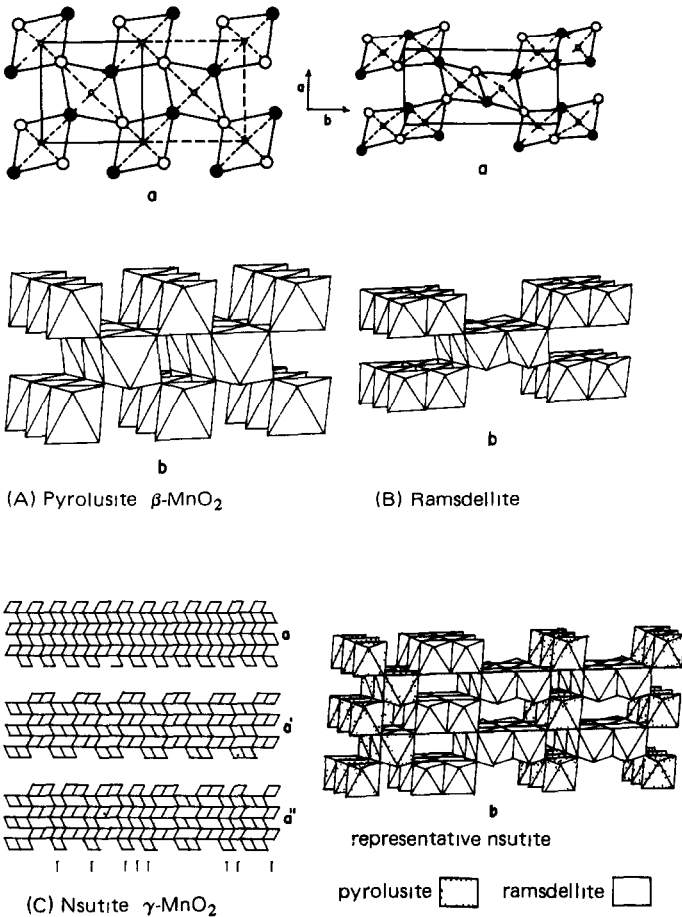


Fig 1 Crystal structures of the manganese dioxides. In each case, schema marked a represent (001) projections of the [MnO<sub>6</sub>] linked octahedra and those marked b represent three-dimensional representations of the same. In Fig 1(C), a, a' and a'' represent (001) projections of pyrolusite, ramsdellite and intergrown pyrolusite and ramsdellite domains, respectively.

the other half sharing only one face [244]. In general, the overall linking of the  $[\text{MnO}_6]$  octahedra determines the particular crystal phase of  $\text{MnO}_2$  [238]. Ramsdellite, a dimorph of pyrolusite [240], is built of alternating double chains of linked octahedra which are further cross-linked to adjacent double chains through corner sharing of oxygen atoms and departs from stoichiometry more than does  $\beta\text{-MnO}_2$ . It is rare in nature and its chemical synthesis is patented [115], although some earlier reports claim its synthesis by oxidation of synthetic groutite [94, 95]

### 5.3 *Nsutite or the $\gamma\text{-MnO}_2$ group*

This group is non-stoichiometric with  $\text{Mn}^{3+}$  replacing  $\text{Mn}^{4+}$  and with  $\text{OH}^-$  replacing  $\text{O}^{2-}$ , right up to the end member  $\text{MnOOH}$ . It is, therefore, difficult to recognize one particular variety or member of this group solely on the basis of routine X-ray investigations. The composite influence of crystallite size, intergrowth lattice disorder and partial substitution of  $\text{Mn}^{4+}$  by  $\text{Mn}^{3+}$  may produce a wide variety of X-ray patterns within the same group of compounds. These factors are also responsible for the asymmetric and selective line broadening. From detailed analysis of some line-rich  $\gamma\text{-MnO}_2$  patterns, de Wolff [249] has shown that the position of the sharper lines is in perfect accordance with a ramsdellite type of lattice. Certain broad lines, however, are shifted away from the positions consistent with the sharper lines in the same pattern. Both the anomalous broadening and the shift are satisfactorily explained on the basis of a structural model consisting of randomly alternating layers of ramsdellite and pyrolusite units. In view of this random structural intergrowth, regular periodicity or a superlattice is not apparent. Such lattice disorder causes nsulites and synthetic  $\gamma\text{-MnO}_2$  phases to have extensive defects and vacancies as well as to be non-stoichiometric and impure [250]. These factors, together with the small crystallite sizes of natural and synthetic phases, give rise to a variety of X-ray powder diffraction lines, as well as the observed asymmetric and selective line broadening for nsulites.

de Wolff's model [249, 251] briefly assumes a diaspore matrix with random slices of one unit cell thickness of the rutile type-structure. According to de Wolff and Giovanoli and co-workers [251, 252], however, electrolytic  $\text{MnO}_2$  does not belong to this group and they were the first to interpret EMD as  $\epsilon\text{-MnO}_2$ . Further, they are of the opinion that ramsdellite, i.e. purely diaspore-type  $\text{MnO}_2$ , without intergrowth, cannot be produced electrolytically. According to Preisler [253], there should be two OH groups for every eight  $\text{Mn}^{4+}$  ions. If this is the case, the models proposed by Bystrom as well as by de Wolff appear to be inadequate. This conclusion is supported by the log of the conductivity being inversely proportional to the water content of the manganese dioxides. If the electrons are transported by a hopping mechanism between neighbouring manganese orbitals, the d.c. conductivity should decrease if the interatomic spacing between the Mn ions is increased by lattice expansion in the direction of the current. This is caused by the incorporation of additional oxygen

in the form of OH groups. On heating, the OH groups become detached and the domains of pyrolusite randomly distributed within the sample would re-appear. The now shorter Mn-Mn distances will result in an increased probability of tunnelling, and thus explain the increased conductivity with the progressive increase in the pyrolusite domains. These observations of Preisler are apparently supported by the X-ray diffraction studies on fibrous electrolytic MnO<sub>2</sub> of Freund and co-workers [254], wherein it is proposed that  $\gamma$ -MnO<sub>2</sub> consists of two pyrolusite-type cells joined in the  $a/b$  plane containing one additional OH<sup>-</sup> ion in the centre. On the basis of an orthorhombic unit cell, the lattice parameters evaluated were  $a = 4.85$ ,  $b = 8.90$  and  $c = 2.80$  Å. They also described the structure in terms of a super cell with the same  $a$  and  $b$  values as above but with  $c = 8.4$  Å. The observation that EMD does not match the X-ray data of  $\gamma$ -MnO<sub>2</sub> was first made by these workers.

Parida *et al* [255] are apparently not satisfied with the above observations of Preisler and co-workers [253, 254], especially with regard to their assumption of an orthorhombic unit cell for  $\gamma$ -MnO<sub>2</sub> which should contain two manganese, eight oxygen atoms and one OH group [254]. Care has to be taken, however, when interpreting the presence of a  $\beta$ -MnO<sub>2</sub> peak in the X-ray diagram of EMD, which can sometimes be found. EMD may contain  $\beta$ -MnO<sub>2</sub> as a discrete phase and not associated with the electrochemical formation of EMD. It can be ascribed to the presence of MnSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> at high solution temperatures.

Parida *et al* [255] investigated  $\gamma$ -manganese dioxides from various sources and characterized them by chemical analysis, pycnometric density measurements and unit cell volumes based on crystal lattice parameters. They observed a difference of one formula unit (MnO<sub>2</sub>· $x$ H<sub>2</sub>O) per unit cell between the empirical formula obtained from chemical analysis and the one derived on the basis of an orthorhombic unit cell. They explained the X-ray patterns of powdered  $\gamma$ -MnO<sub>2</sub> on the basis of a hexagonal crystal system. Even the line at  $d_{hkl} = 3.1$  Å, which could not be explained on the orthorhombic system, could be on the basis of the hexagonal crystal class. Whether or not  $\gamma$ -MnO<sub>2</sub> can be indexed on the basis of an orthorhombic or a hexagonal system still remains unresolved. In this context, it needs to be pointed out that Giovanoli [256] demonstrated the presence of the  $\beta$  line in a  $\gamma$ -MnO<sub>2</sub> sample. The  $d_{hkl} = 3.1$  Å line, therefore, need not necessarily be explained away if the presence of  $\beta$  microdomains is confirmed.

#### 5.4 The $\gamma$ -MnO<sub>2</sub> group

It is interesting to note that electrolytic manganese dioxide (EMD) is not a  $\gamma$ -MnO<sub>2</sub>, as is usually assumed, but consists of a hexagonal close-packed lattice of O<sup>2-</sup> ions in which half the octahedral sites are almost filled at random by Mn<sup>4+</sup> ions, implying that some face-shared [MnO<sub>6</sub>] octahedra may occur in EMD. de Wolf *et al*, in 1978 [251], made this observation after investigating the oriented texture patterns of an EMD synthesized by Preisler [253]. The EMD is referred to as  $\epsilon$ -MnO<sub>2</sub>. Giovanoli



[256] reported that  $\epsilon$ - $\text{MnO}_2$  is also obtained by the oxidation of acidified  $\text{Mn}(\text{NO}_3)_2$  solution with ozone. According to him [257], the face-sharing octahedra cannot be occupied by  $\text{Mn}^{4+}$  ions as it would result in an extremely short Mn–Mn distance. This would imply a strong cation–cation repulsion. In the  $c$  direction, therefore, there is a regular alternating sequence (–full–empty–full–empty–) of these sites while each layer is itself randomly filled. This feature produces a diffuse reflection in the region of 4.22 Å, and is often confused with the 110 reflection of  $\gamma$ - $\text{MnO}_2$ , although it is clearly displaced.  $\epsilon$ - $\text{MnO}_2$  is referred to as a thermodynamically metastable state as it is easily recrystallized to  $\gamma$ - $\text{MnO}_2$  in hot 2 M nitric acid [257]. Although disordered, EMD has no amorphous portions and is formed only under the particular conditions of high current density, fast nucleation and limited growth, *i.e.* when there is no chance of reaching thermodynamic equilibrium.

Giovanoli [256] also investigated  $\epsilon$ - and  $\gamma$ - $\text{MnO}_2$  by subjecting them to mild topotactical reduction by the method of Gabano *et al* [258] which uses cinnamic alcohol in xylene for the chemical reduction. X-ray analysis showed that  $\gamma$ - $\text{MnO}_2$  reduced to  $\alpha$ - $\text{MnOOH}$  having a few microdomains of  $\gamma$ - $\text{MnOOH}$  in its matrix, while  $\epsilon$ - $\text{MnO}_2$  reduced to  $\gamma$ - $\text{MnOOH}$ . The latter fact was explained on the grounds that rutile-type microdomains operate as nuclei for  $\gamma$ - $\text{MnOOH}$  when reduction occurs. Conversely, under mild oxidation with dry air or  $\text{O}_2$ , which ensures the topotactical nature of the reaction,  $\alpha$ - $\text{MnOOH}$  oxidized to  $\gamma$ - $\text{MnO}_2$  and  $\gamma$ - $\text{MnOOH}$  to  $\beta$ - $\text{MnO}_2$ . With strong oxidation  $\beta$ - $\text{MnO}_2$  was the product in both cases. During reduction, when almost half the reaction was over, Jahn–Teller distortion of the  $[\text{MnO}_6]$  octahedra began to be observed owing to the increasing number of  $\text{Mn}^{3+}$  ions which are formed [256]. The effect of heat treatment on EMD ( $\epsilon$ - $\text{MnO}_2$ ) and CMD ( $\gamma$ - $\text{MnO}_2$ ) has also been studied [256, 259]. Giovanoli [256] observed that EMD reacted very slowly to heat treatment, *i.e.* without forming much  $\beta$ - $\text{MnO}_2$ , compared to CMD. This was believed to be due to the possible presence of  $\text{SiO}_2$  in EMD, for which there is a little evidence, which could suppress its nucleation to  $\beta$ - $\text{MnO}_2$ , the role of  $\text{SO}_4^{2-}$  in this process, however, was not considered. It was also observed [256, 260] that EMD produced in chloride and sulphate baths has different properties. The role of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in the process, however, is not understood. The absence of a peak of  $\theta = 14^\circ$  (Fe  $K\alpha$ ) in CMD, considered to have a  $\gamma$ - $\text{MnO}_2$  structure, is still unexplained [260, 261].

The dimension of the tunnels (although whether it is a tunnel structure or a layer structure is a controversial point) in the  $\text{MnO}_2$  structures is represented as  $[1 \times 1]$  for pyrolusite,  $[1 \times 2]$  for ramsdellite, and so on for other structures depending upon the stacking of the  $[\text{MnO}_6]$  octahedral chains around the tunnel involved [250]. On the basis of the newly discovered intergrowths of multidimensional tunnels in naturally occurring Mn(IV) oxides by high resolution transmission electromicroscopy (HRTEM) techniques [262], a revised nomenclature for Mn(IV) oxides was suggested [250] which, in general, was to use  $T(m, n)$ . Thus, pyrolusite is  $T(1, 1)$  and ramsdellite  $T(1, 2)$  so that  $\gamma$ - $\text{MnO}_2$  and  $\epsilon$ - $\text{MnO}_2$  might be repre-

sented as T(1, 1)-T(1, 2) intergrowths. As  $n$  increases, a tunnel structure approaches a layer structure. Incoherent intergrowths of bunches of unit cells containing simple and multidimensional tunnels lead to the trapping of mother liquors containing  $H_2O$ , cations ( $Na^+$ ,  $K^+$ ) and anions ( $SO_4^{2-}$ ,  $NO_3^-$ ,  $ClO_4^-$ ) in large tunnels, defects and voids at grain boundaries. These gross structural imperfections explain why  $\gamma$ - $MnO_2$  and  $\epsilon$ - $MnO_2$  have such high water contents (typically 4 - 6 wt.%  $H_2O$ ), porosities and specific surface areas which cannot be accounted for given a rigid perception of the crystal structures [251, 263]. The HRTEM used to investigate multidimensional tunnels in natural dioxides, if applied to chemically and electrolytically synthesized manganese dioxides obtained from various sources, may give a better insight into the subtle structural features of the dioxides [264].

### 5.5 The $\alpha$ - $MnO_2$ group

The structure of  $\alpha$ - $MnO_2$  involves the cross-linking of double chains of  $[MnO_6]$  octahedra [238, 265], resulting in tunnels of  $2 \times 2$  dimension (Fig. 2). The structure is stabilized by the incorporation of large cations, usually with radii up to 1.35 Å such as  $K^+$ ,  $Ba^{2+}$ ,  $NH_4^+$ , into the tunnels

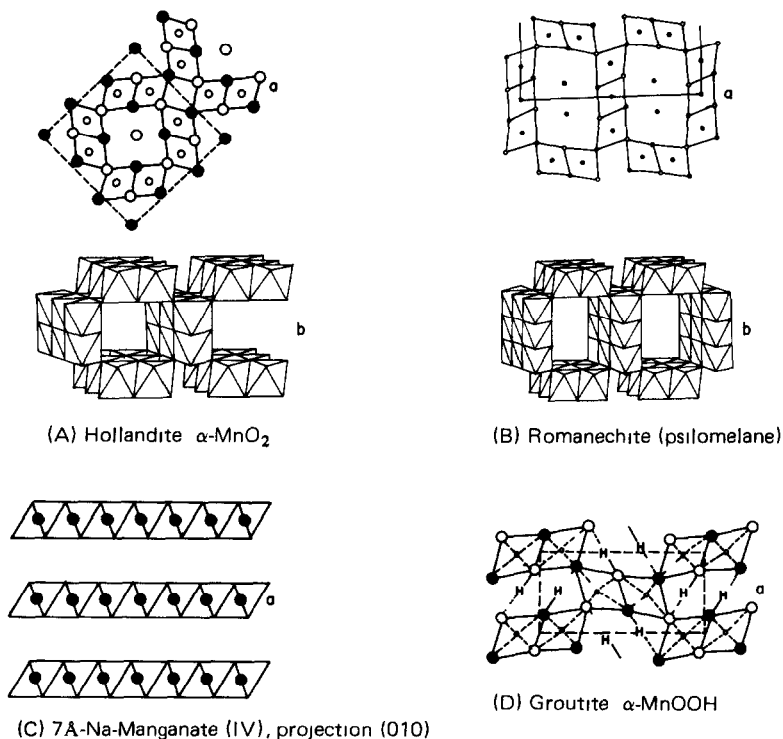


Fig. 2 Crystal structures of manganese dioxides and oxyhydroxides (a and b are as in Fig. 1)

[266]. These tunnels, however, do not exist *a priori* [256], but are apparently a consequence of simultaneous entry of the cation during the process of crystallization of the  $\alpha$  phase. The reports [255, 266, 267] that  $\alpha$ - $\text{MnO}_2$  can also be obtained in the absence of such cations seem to be misguided as the authors concerned have apparently ignored the presence of  $\text{NH}_4^+$  ions in the reaction medium [256]. For charge balance, some of the  $\text{Mn}^{4+}$  ions must be replaced by vacancies or lower valence cations of similar ionic radius. While the presence of cations can adversely affect the battery performance, there are reports of the synthesis of  $\alpha$ - $\text{MnO}_2$  having high electrochemical activity, such as the one obtained by the action of  $\text{HCl}$  on  $\text{KMnO}_4$  [135].

Dubois [133] was probably one of the first to attempt a structural investigation of  $\alpha$ - $\text{MnO}_2$  obtained by the chemical reduction of  $\text{KMnO}_4$ . Richmond and Fleischer [268] and McMurdie [269] later studied its properties and differentiated it from other  $\text{MnO}_2$  polymorphs. The general formula for the  $\alpha$  phases  $\text{A}_{2-y} \text{B}_{8-y} \text{X}_{16}$  where  $\text{A}$  = large ions, *e.g.*  $\text{K}^+$ ,  $\text{X} = \text{O}^{2-}$  or  $\text{OH}^-$ , and  $\text{B}$  = small ions, *e.g.*  $\text{Mn}^{4+}$  [270] or  $x < 1$  in the general formula of the type  $\text{A}_x \text{Mn}_8 \text{O}_{16}$  [271]. The general formula of the  $\alpha$ - $\text{MnO}_2$  was believed to be similar to that of the naturally occurring minerals cryptomelane ( $\text{K}^+$ -containing phase) and hollandite ( $\text{Ba}^{2+}$ -containing phase). Their designation as  $\alpha$ - $\text{MnO}_2$ , however, was considered to be incorrect by Giovanoli [256] as these do not have the required stoichiometry and cannot, therefore, be regarded as a modification of  $\text{MnO}_2$ . The structure of the mineral psilomelane (romanéchite) involves the cross-linking of double and triple chains of  $[\text{MnO}_6]$  octahedra [243] with the incorporation of  $\text{Ba}^{2+}$  and  $\text{H}_2\text{O}$  in the ratio 1.2 in the tunnels [272], although some  $\text{Ba}^{2+}$  sites are vacant. The Bystroms [265] indexed the minerals hollandite and psilomelane on the basis of a monoclinic unit cell with dimensions  $a = 9.9 \text{ \AA}$ ,  $b = 2.87 \text{ \AA}$ ,  $c = 9.9 \text{ \AA}$  and  $\beta = 90.6^\circ$ . They indexed synthetic  $\alpha$ - $\text{MnO}_2$  on the basis of a tetragonal unit cell with the approximate dimensions  $a = b = 9.8 \text{ \AA}$ ,  $c = 2.85 \text{ \AA}$ . Delano [273] and Maxwell *et al* [274] reported the existence of monoclinic cryptomelane with  $a = 9.79 \text{ \AA}$ ,  $b = 2.86 \text{ \AA}$ ,  $c = 9.94 \text{ \AA}$  and  $\beta = 90.37^\circ$ . Black, needle-like single crystals of  $\alpha$ - $\text{MnO}_2$  were synthesized by heating a mixture of  $\gamma$ - $\text{MnOOH}$  and  $\text{KOH}$  for a week at  $650^\circ \text{C}$  under a hydrostatic pressure of  $1650 \text{ kg/cm}^2$ , followed by quenching at room temperature [267]. X-ray studies indicated that the  $\alpha$ - $\text{MnO}_2$  was monoclinic with space group  $\text{C}_{2h}^3$ , having the longest axis of the crystal parallel to the crystal  $c$ -axis. The effect of several cations on the formation of  $\alpha$ - $\text{MnO}_2$  was studied after  $\alpha$ - $\text{Mn}_2\text{O}_3$  and an acid mixture (3 N  $\text{HOAc}$  + 8 N  $\text{HNO}_3$ ) were reacted. It was observed that in the presence of  $\text{NH}_4^+$ , the  $\alpha$ - $\text{MnO}_2$  showed a remarkable crystal growth [275]. Recent studies by Post *et al* [276] and by Bursill and Grzanic [277] indicated that there is a superlattice ordering in hollandites which is incommensurate, *i.e.* the long-range periodicity impressed on the substructure has no apparent spatial relationship to the substructure periodicity.

### 5.6 The phyllo-manganates or the so-called $\delta$ - $\text{MnO}_2$ group

Finely divided oxides of manganese having prominent diffractions near  $d_{hkl} = 1.42, 2.44, 3.63$  and  $7.3 \text{ \AA}$  have been obtained by alkaline oxidation of manganous hydroxide [278] as well as by the decomposition of permanganates with hydrochloric acid [137]. These are known as phyllo-manganates or Mn(IV) oxides with layer structures containing infinite two-dimensional sheets of edge-shared  $[\text{MnO}_6]$  octahedral and separated by  $7 \text{ \AA}$  or  $10 \text{ \AA}$  [256]. Intermediate layers may contain sheets of  $\text{H}_2\text{O}$  molecules or  $\text{OH}^-$  ions bonded to the  $[\text{MnO}_6]$  octahedral layers by  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Na}^+$ , etc., ions. Cation vacancies may exist in the sheets of edge-shared  $[\text{MnO}_6]$  octahedra, and these  $\text{Mn}^{4+}$  vacancies may or may not be ordered. Stacking disorder between the octahedral layers and the random existence of  $\text{Mn}^{2+}$  vacancies with different cations adjacent to them are reported to be characteristic features of Mn(IV) oxides with layer structures [250]. It is also reported that these compounds readily scavenge divalent metal ions, to exchange these against  $\text{Na}^+$  and  $\text{Mn}^{2+}$  ions and to incorporate the exchanged ions into the lattice [256]. These phyllo-manganates also occur in nature. The  $10 \text{ \AA}$  phyllo-manganates known as busserites are the hydrates of  $7 \text{ \AA}$  phyllo-manganates or the birnessites. Rehydration of the former does not, apparently, occur [256]. To name these oxides as  $\delta$ - $\text{MnO}_2$  is considered to be incorrect, as they are not true modifications of  $\text{MnO}_2$  [256]. There is no general consensus, however, on their nomenclature, although many of the investigations were reported earlier on [67, 73, 90, 139, 278 - 286].

The natural as well as the synthetic forms of these oxides contain less than the stoichiometric proportion of oxygen. Busser *et al* [67] recommended that the particular phase be called "manganous manganite" or  $\delta$ - $\text{MnO}_2$ , depending upon whether the O:Mn ratio was less than or greater than 1.9. They attributed the different diffraction patterns of some members of this group to the disordering of the structure when the  $\text{Mn}^{2+}$  ions in the intermediate layer of manganous manganite were oxidized, thus removing the  $\text{Mn}(\text{OH})_2$  sheets and the periodicity of the basal planes. Bricker [281], however, suggested that the presence or absence of the basal planes is a function of particle size. He recommended that the name "manganous manganite" be dropped and  $\delta$ - $\text{MnO}_2$  alone be retained. Giovanoli *et al* [284] showed, on the basis of high resolution electron diffraction and X-ray diffraction techniques, that certain synthetic "manganous manganite" phases, reported by earlier workers, contain sodium like natural birnessites. The analytical formula recommended by them is  $\text{Na}_4\text{Mn}_{14}\text{O}_{27} \cdot 9\text{H}_2\text{O}$ . They named this sodium manganous(II, III) manganate(IV), believed to have an orthorhombic superlattice. Giovanoli *et al* [285] also suggested that the synthetic birnessite group, by analogy with the nsutite group, consists of an infinite number of varieties with one and the same crystal lattice.

Recently, R.G. and V. M. Burns [250] classified these oxides (birnessites and busserites), among others, with respect to their chemical formulae, crystal class, space group, lattice cell parameters, and other structural

features. According to Burns and Burns [238], the  $\delta$ - $\text{MnO}_2$  phase is generally considered to be a disordered variety of birnessite. Its X-ray patterns, however, contain only two broad diffuse lines at about 2.40 Å and 1.42 Å, with little or no suggestion of the lines at 7.0 - 7.2 Å and 3.5 - 3.6 Å, which are diagnostic basal plane reflections for birnessite. Recent extended X-ray absorption fine structure (EXAFS) measurements on birnessites and busserites yielded details of  $\text{Mn}^{4+}$  site vacancies and co-ordination environments for cations  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , etc., situated adjacent to these vacancies [287, 288]. These measurements showed that the cations are bound in the birnessite structure and are not randomly absorbed on external surfaces of the micro-crystallites. The subtle distinction between tunnel and layer structures in Mn(IV) oxides seems to be governed by the relative magnitude of the values of  $x$  in the system  $\text{K}_x\text{MnO}_2$  and  $\text{Na}_x\text{MnO}_2$  where  $x \leq 1$ . Thus the potassium Mn oxide with  $x = 0.25$  (cryptomelane, isostructural with  $\alpha$ - $\text{MnO}_2$ ) has a tunnel structure, whereas  $x = 0.70$  corresponds to a layer structure in which  $\text{K}^+$  ions link sheets of  $[\text{MnO}_6]$  octahedra 6.25 Å apart [289]. The content of co-ordinated water and unco-ordinated hydrate water, as well as the presence of  $\text{Mn}^{2+}$  and/or  $\text{Mn}^{3+}$  ions, seem to limit the usefulness of the phyllosulfate group of Mn(IV) oxides to the battery industry [256]. They are usually characterized by a high voltage but a short life [237]. These can, however, be transformed to  $\gamma$ - $\text{MnO}_2$  by heat treatment or by being digested in  $\text{HNO}_3$  under reflux conditions and in the absence of  $\text{K}^+$  ions. A 7 Å phyllosulfate having an analytical composition  $\text{Mn}_7\text{O}_{13} \cdot 5\text{H}_2\text{O}$  can be synthesized by the careful leaching of  $\text{Na}^+$  ions with dilute  $\text{HNO}_3$ , which also includes oxidation of the remaining  $\text{Mn}^{2+}$  ions to  $\text{Mn}^{3+}$  [256]. This oxide can be topotactically reduced to  $\gamma$ - $\text{MnOOH}$  by the use of cinnamic alcohol in xylene.

The oxyhydroxides of manganese are also considered as important compounds in the crystal chemistry of manganese dioxides, they are the main products of the electrochemical reduction of the dioxides, and are also considered to be present as  $\text{MnOOH}$  groups.  $\alpha$ - $\text{MnOOH}$  (groutite) is known to be isostructural with ramsdellite and consists of double chains of linked  $[\text{Mn}(\text{O}, \text{OH})_6]$  octahedra [238, 290] in which hydrogen bonding also plays a significant role. It is considered to be the dominant reduction product of  $\gamma$ - $\text{MnO}_2$ . Manganite ( $\gamma$ - $\text{MnOOH}$ ) is usually the reduction product of pyrolusite. Feitknechtite ( $\beta$ - $\text{MnOOH}$ ) is obtained by the oxidation of pyrochroite, i.e.  $\text{Mn}(\text{OH})_2$  [238].

### 5.7 Summary of X-ray diffraction

Further investigation could be directed towards the determination of exact amounts of discrete  $\beta$ - $\text{MnO}_2$  in  $\gamma$ - $\text{MnO}_2$  phases. What exactly distinguishes a chemical  $\gamma$ - $\text{MnO}_2$  from an electrolytic  $\text{MnO}_2$  is still not clear. According to Giovanoli (personal communication), however, there is no fundamental difference between CMD and EMD, but  $\gamma$ - $\text{MnO}_2$  exists in an infinite number of varieties, both synthetic and natural, and EMD is one of them. CMD can also have many different appearances in crystal growth, shape, order/disorder, etc.

## 6. Conclusion

Research on the synthesis of manganese dioxides continues to evoke considerable interest, mainly due to its ever-increasing demand in the battery industry as an active cathode material. Increasing importance is given to the chemical synthesis of the dioxides as a substitute for the relatively expensive electrolytically synthesized dioxides which are almost exclusively used at present for high quality dry cells. Although highly active chemical manganese dioxides have been synthesized by various workers, they have not found much favour with the battery manufacturers on account of their comparatively low tap density and also relatively low open-circuit voltage in alkaline manganese dioxide batteries. The above factors, as well as the cost of manufacture, should be taken into consideration in future research on the chemical synthesis of manganese dioxides

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## List of symbols

$a, b, c$	crystal lattice parameters
$d_{hkl}$	interplanar distance
$C_{2h}^3$	space group
$\alpha, \beta, \gamma, \delta, \lambda, \eta, \epsilon, \rho$	various MnO <sub>2</sub> polymorphs
$\theta$	Bragg diffraction angle

## References

- 1 G Leclanché, *Le Monde*, 16 (1868) 532, *C R Acad Sci*, 83 (1876) 54
- 2 G W Heise and N C Cahoon, *J Electrochem Soc*, 99 (1952) 179C
- 3 G K Morehouse, *J Electrochem Soc*, 99 (1952) 187C
- 4 W S Herbert, *J Electrochem Soc*, 99 (1952) 190C
- 5 A D Wadsley and A Walkley, *Rev Pure Appl Chem*, 1 (1951) 203
- 6 J Brenet, *Bull Soc Fr Minéral Crystallogr*, 77 (1954) 797
- 7 W Buser and P Graf, *Helv Chim Acta*, 38 (1955) 810
- 8 W C Vosburgh, *J Electrochem Soc*, 106 (195) 839
- 9 M A Malati, *Chem Ind (London)*, (1971) 446-452
- 10 S B Kamungo and B R Sant, *J Sci Ind Res*, 31 (1972) 264

- 11 K V Kordesch (ed), *Batteries Vol 1, Manganese Dioxide*, Marcel Dekker, New York, 1974
- 12 G W Heise and N C Cahoon (eds), *The Primary Battery*, Vol 1, Wiley, London, 1971
- 13 N C Cahoon and G W Heise (eds), *The Primary Battery*, Vol 2, Wiley, London, 1976
- 14 F L Tye, in M Barak (ed), *Primary Batteries for Civilian Use Electrochemical Power Sources*, Peter Peregrinus, London, 1980, pp 50 - 150
- 15 K Takahashi, S Yoshizawa and A Kozawa (eds), *Electrochemistry of Manganese Dioxide and Manganese Dioxide Batteries in Japan*, US Branch Office, Electrochem Soc Jpn, Cleveland, OH, 1971
- 16 A Kozawa and R J Brodd (eds), *MnO<sub>2</sub> Symp Proc*, Cleveland, OH, 1 (1975)
- 17 B Schumm, Jr, H M Joseph and A Kozawa (eds), *MnO<sub>2</sub> Symp Proc*, 2 (1980)
- 18 A Kozawa et al (eds), *Prog Batteries Sol Cells*, 1 (1978), 2 (1979), 3 (1980), 4 (1982)
- 19 A Kozawa, *MnO<sub>2</sub> Symp Proc*, 2 (1980) 321 - 334
- 20 K Takahashi, *Electrochim Acta*, 26 (1981) 1467 - 1476
- 21 K Takahashi, *Prog Batteries Sol Cells*, 3 (1980) 140 - 156
- 22 K Kordesch and J Gsellmann, *J Electroanal Chem Interfacial Electrochem*, 118 (1981) 187 - 201
- 23 J Koshiba, *Gendai Kagaku*, 94 (1979) 48 - 52
- 24 Ya A Braker, *Khim Promst*, Ser Fosformaya Promst, 4 (1980) 22 - 23
- 25 H Kobayashi and A Kozawa, *Kinzoku Sankabutsu to Fukugo Sankabutsu*, (1978) 215 - 229
- 26 E Preisler, *Chem Unserer Zeit*, 14(5) (1980) 137 - 138
- 27 Z M Buzowa and R P Sobolev, *Elektrotekh Promst*, *Khim Fiz Istokhimi* *Toka*, 1 (1982) 6 - 8
- 28 C R Talpade, S M Dõnde and P G Pradhan, *Chem Era*, 12(8) (1976) 317 - 325
- 29 A J Fatiadi, *Synthesis*, 2 (1976) 65 - 104
- 30 A Gargeu, *Bull Soc Minéral Fr*, 2 (1879) 122
- 31 J P Brenet and N Busquire, *C R Acad Sci*, 230 (1950) 1767
- 32 T E Moore, M Ellis and P W Selwood, *J Am Chem Soc*, 72 (1950) 856
- 33 O Glemser and H Meisiek, *Z Angew Chem*, 69 (1959) 534
- 34 O Glemser and H Meisiek, *J Pract Chem*, 5 (1958) 219
- 35 L Pons and J P Brenet, *C R Acad Sci*, 260 (1965) 2483
- 36 L Pons and J P Brenet, *C R Acad Sci*, 259 (1964) 2825
- 37 A A Azim, G H Kolla and M H Askar, *Electrochim Acta*, 17 (1972) 291
- 38 K H Marwell and H R Thirsk, *J Chem Soc*, (1955) 5057
- 39 R M McKenzie, *Mineral Mag*, 38 (1971) 493
- 40 E S Nossen, *US Pat* 2,681,268 (15 Jun 1954), *Chem Abstr*, 48 (1954) 13185
- 41 N K Videnov, L K Hristova and L Dimitrova, *God Nauchnoizsled Inst Khim Promst*, 8 (1970) 31
- 42 N K Videnov and D L Dimitrov, *Marganets*, 1 (1971) 93, *Chem Abstr*, 80 (1974) 85185p
- 43 B I Barachyi, F R Andryushchenko, T P Yaroshok and L V Lyashok, *Zh Prikl Khim (Leningrad)*, 48(7) (1975), *Chem Abstr*, 83 (1975) 154480
- 44 M B Kudelina, *Sb Nauchn Stud Ova Geol Fak Mosk Gos Univ*, 10 (1974) 92, *Chem Abstr*, 83 (1975) 36894x
- 45 O P Molchanova, L V Kozinnayo and V M Markova, *Chem Abstr*, 89 (1978) 183041
- 46 S S Markov and L B Belyaeva, *Chem Abstr*, 90 (1979) 1613446r
- 47 I Harelmann and H Funk, *Fr Pat*, 1,540,654 (27 Sep 1968), *Chem Abstr*, 69 (1968) 83100
- 48 F G Kretschmer, *Ger Offen*, 2,333,532 (23 Jun 1975), *Chem Abstr*, 82 (1975) 158610p

- 49 S S Markov, G A Seryshov, N M Surova and N M Yakovleva, *USSR Pat*, 513,937,15 (Apr 1974)
- 50 J Y Welsh, *PCT Int Appl*, 80,02,555 (27 Nov 1980), *Chem Abstr*, 94 (1981) 195686
- 51 P Faber, *Chem -Ing -Tech*, 49 (1977) 333
- 52 Fuji Electrochemical Co Ltd, *Jpn Kokai Koho*, 81, 164, 017 (16 Dec 1981)
- 53 M W Rophael, T A Bibawy, L B Khalil and M A Malati, *Chem Ind*, (1979) 29
- 54 L B Khalil, *M Sc Thesis*, Cairo University, 1979
- 55 W E Mourad, M W Rophael and L B Khalil, *J Appl Electrochem*, 10 (1980) 309
- 56 J P Brenet, *C R Acad Sci*, 247 (1958) 783
- 57 T Valand, *J Power Sources*, 1 (1976) 65
- 58 A Simon and F Feter, *Kolloid Z*, 14 (1931) 50 - 58
- 59 A Simon and F Feter, *Z Elektrochem*, 38 (1932) 137 - 148
- 60 A R Nichols and J H Walton, *J Am Chem Soc*, 64 (1942) 1866
- 61 L C Copeland, E S Griffith and C B Schertzing, *Trans Electrochem Soc*, 92 (1947) 22
- 62 U C Agarwala, N R Sanjana and J Gupta, *Indian Pat*, 54, 395 (to Council of Sci and Ind Res, New Delhi) (3 May 1955)
- 63 W Feitknecht, H R Oswald and U Feitknecht-Steinmann, *Helv Chim Acta*, 43 (1960) 1947 - 1949
- 64 J P Brenet, *Fr Pat*, 1,306,706 (to Société Les Piles Wonder 1) (1962)
- 65 R W Walton, *US Pat* 2,459,714 (to Manganese Prod Inc) (18 Jan 1949)
- 66 A D Wadsley, *J Am Chem Soc*, 72 (1950) 856
- 67 W Buser, P Graf and W Feitknecht, *Helv Chim Acta*, 37 (1954) 322
- 68 M Beley and J P Brenet, *Electrochim Acta*, 18 (1973) 1003
- 69 G Y Szigetı and P Kaldi, *Proc Conf Appl Phys Chem*, 2 (1971) 575
- 70 V A Stepanov *et al*, *Chem Abstr*, 92 (1980) 131526y
- 71 K Tanaka and I Watanabe, *Jpn Kokai*, 74,84,995 (15 Aug 1974)
- 72 T Shramoto, *Jpn Kokai*, 7510,300,1 (Feb 1975)
- 73 R Giovanoli and U Leuenberger, *Helv Chim Acta*, 52 (1969) 2333
- 74 J P Brenet, Plı Cacheté No 13 408 déposé à l'Acad Sci, Paris (1955)
- 75 J P Brenet and A Grund, *C R Acad Sci*, 242 (1956) 2343
- 76 J P Brenet, *C R Acad Sci*, 243 (1956) 1310
- 77 J P Brenet, G Coeffier and J P Gabano, *C R Acad Sci*, 254 (1962) 2552
- 78 G Perrault, J P Brenet and G Coeffier, *C R Acad Sci*, 258 (1964) 1226
- 79 J P Brenet, *Proc 4th Int Symp on Batteries, Brighton, 1964*, Pergamon, London, 1965
- 80 L Balewski, J Brenet and G Coeffier, *C R Acad Sci*, 262 (1966) 172
- 81 H Purol, A Nowackı and J P Brenet, *C R Acad Sci*, 267 (1968) 429
- 82 J P Brenet, H Purol and A Nowackı, *C R Acad Sci*, 267 (1968) 1749
- 83 J P Brenet, *Brevet Français*, 1,306,706 (1961) and 1,525,333 (1956)
- 84 J P Brenet, Plı Cacheté No 12,847 déposé à l'Acad Sci, Paris (1951)
- 85 I S Morozov and V G Kuznetsov, *Chem Abstr*, 44 (1950) 65, *Izv Akad Nauk SSSR Otd Khim Nauk*, (1949) 343
- 86 H Purol, *Przem Chem*, 54(6) (1975) 345
- 87 P Faber, *Ph D Thesis*, Université Louis Pasteur, Strasbourg, France, 1976
- 88 C Mitsurada *et al*, *Kagoshima Daigaku, Kogakubu Kenkyu Hokoku*, 22 (1980) 125 - 31
- 89 M Beley and J P Brenet, *C R Acad Sci, Ser C*, 273 (1971) 1137
- 90 R Giovanoli, R Maurer and W Feitknecht, *Helv Chim Acta*, 50 (1967) 1072
- 91 R Giovanoli, E Staehli and W Feitknecht, *Chimia*, 23 (1969) 246
- 92 R Giovanoli, W Feitknecht, W Maurer and R Haeni, *Chimia*, 30 (1976) 307
- 93 R K Sorem and E N Cameron, *Econ Geol*, 55 (1960) 278
- 94 A F Wells, *Structural Inorganic Chemistry*, Clarendon Press, London, 1947
- 95 P Faber and J P Brenet, *Ger Offen*, 2,419,490 (30 Oct 1975)



- 96 P Faber and J P Brenet, *Ger Offen*, 2,454,012 (26 May 1976)
- 97 S Chatterjee, *Br Pat*, 615,980 (14 Jan 1949)
- 98 N S Krishnaprasad, *J Indian Inst Sci*, Sect A, 36 (1954) 19
- 99 W G Moore, *US Pat*, 3,356,452 (5 Dec 1967), *Chem Abstr*, 68 (1968) 31633
- 100 Cited in *MnO<sub>2</sub> Symp Proc*, Cleveland, OH, 1 (1975) *US Pat*, 2,608,466 (26 Aug 1952), *US Pat*, 2,757,071 (31 Jul 1956), *Jpn Pat*, 36-16413 (15 Sep 1961), *US Pat*, 3,647,375 (7 Mar 1972), *Jpn Pat*, 40-736 (16 Jan 1965)
- 101 I Tanabe and T Honda (Nippon Inkagaku Kogyo Ltd) *Jpn Pat*, 74 27,277 (16 Jul 1974)
- 102 M G Bodas, *Trans Indian Inst Met*, 32 (1979) 415
- 103 G G Tarakanouski, N M Vinnikov, G G Gorovoi, N M Kamenskaya, Yu L Ponomarov and O A Tarakanovskaya, *USSR Pat*, 833,543 (30 May 1981)
- 104 T Shiramoto, *Jpn Kokai*, 74 109,297 (17 Oct 1974)
- 105 T Hashimoto and Y Hayashi, *Jpn Kokai Koho*, 79 106,099 (20 Aug 1979)
- 106 T Homma and T Yamada, *Kitami Kogyo Tanki Daigaku Kenkyu Hokoku*, 9 (1978) 181
- 107 R S Dean, *Mining Eng*, 4 (1952) 55, (a) J Y Welsh and P Picquet, *Prog Batteries Sol Cells*, 2 (1979) 119
- 108 K Takahashi, *Electrochim Acta*, 26 (1981) 1467
- 109 J Y Welsh, *US Pat*, 3,011,867 (1961)
- 110 I Tanabe, *US Pat*, 3,647,375 (1972)
- 111 I Tanabe, R Nagata and T Watanabe, *MnO<sub>2</sub> Symp Proc*, Tokyo, 2 (1980) 44
- 112 I Tanabe, N Miyamoto, R Nagata, T Watanabe and H Kido, *MnO<sub>2</sub> Symp Proc*, 2 (1980) 59
- 113 J Y Welsh, *US Pat*, 2,956,860 (to Manganese Chemical Corp) (18 Oct 1960)
- 114 Varta-Pertrix Union, GmbH, *Fr Pat*, 1,366,528 (10 Jul 1964)
- 115 A G Greischen, *Br Pat*, 939,240 (9 Oct 1963)
- 116 O Glemser, *Ber Dtsch Chem Ges B*, 72 (1939) 1879
- 117 R Giovanoli, W Feitknecht and P Georges, *Chimia*, 30 (1976) 268
- 118 F A Julian, *J Am Chem Soc*, 15 (1983) 113
- 119 J W Gruner, *Am Mineral*, 28 (1943) 496
- 120 W F Cole, P D Wadsley and A Walkley, *Trans Electrochem Soc*, 92 (1947) 133
- 121 J O Hay, cited in R E Kirk and D F Othmer (eds), *Encyclopedia of Chemical Technology*, Vol 13, Wiley, New York, 1967, p 30
- 122 B D Desai, *Ph D Thesis*, University of Bombay, India, 1980
- 123 C S Brooks, *J Catal*, 4 (1965) 435
- 124 C Kanoh *et al*, *Kenkyu Hokoku Asahi - Garasu Kogyo Gijutsu Shoreikai*, 34 (1979) 187
- 125 G Kanoh, M Takashima and M Takaoka, *MnO<sub>2</sub> Symp Proc*, Tokyo, 2 (1980) 134
- 126 J B Fernades, B D Desai and V N Kamat Dalal, *Electrochim Acta*, 28 (1983) 309
- 127 J B Fernandes, B D Desai and V N Kamat Dalal, *Electrochim Acta*, 29 (1984) 181
- 128 J Y Welsh, *Prog Batteries Sol Cells*, 2 (1979) 119
- 129 A Hertwig, R Hirschberg and H Krampitz, *Ger Offen*, 2,243,841,04 (Apr 1973)
- 130 C R Talpade and P G Pradhan, *Indian Chem Manuf*, 13(11) (1975) 27
- 131 R I Agladze and T G Lezhava, *Soobshch Akad Nauk Gruz SSR*, 101 (1981) 69
- 132 I M Goldman, *J Org Chem*, 34 (1969) 1979
- 133 P Dubois, *Ann Chim*, 5 (1936) 411
- 134 J W Gruner, *Am Mineral*, 28 (1943) 496
- 135 K Yokoyama, T Kawai, O Watanabe and M Takemori, *Jpn Kokai*, 77 128,521 (28 Oct 1977)
- 136 L Berg, J A Davidson and R L Nickelson, *US Pat*, 2,782,098 (to US Army) (19 Feb 1957), *Chem Abstr*, 51 (1957) 16152
- 137 H F McMurdie, *J Electrochem Soc*, 86 (1944) 343

- 138 O Glemser, G Gattow and H Meisick, *Z Anorg Allg Chem*, 309 (1961) 1  
139 K H Maxwell and H R Thirsk, *J Chem Soc*, (1955) 4057  
140 V S Khan and V F Martynova, *Zh Neorg Khim*, 23 (1978) 680  
141 R E Kirk and D F Othmer (eds), *Encyclopedia of Chemical Technology*, Vol 13, Wiley, New York, 2nd edn, 1964, p 9  
142 W Foerst (ed), *Ullmann's Encyclopedia of Technical Chemistry*, Vol 12, Urban and Schwarzenberg, Berlin, 1960, p 225  
143 K J Euler and H Mueller-Helsa, *J Power Sources*, 4 (1979) 77  
144 E Narita and T Okabe, *Bull Chem Soc Jpn*, 53 (1980) 525  
145 B J Mehta and D R Baxi, *Indian J Technol*, 16 (1978) 207  
146 J C Hunter, *J Solid State Chem*, 39 (1981) 142  
147 Y Miyake, cited in K Takahashi, S Yoshizawa and A Kozawa (eds), *Electrochemistry of Manganese Dioxide and Manganese Dioxide Batteries in Japan*, U S Branch Office, Electrochem Soc Jpn, Cleveland, OH, 1971  
148 C G Pigão and J S Pesigan, *Philipp J Sci*, 100 (1971) 189  
149 K I Tischenko, I A Dolotova, E S Sinegribova and O B Dukhovnaya, *Obo-gashch Rud, Chern Metall*, 3 (1975) 93, *Chem Abstr*, 84 (1976) 7831q  
150 E B Sarchinelti, *Geol Metal Bol*, 34 (1974) 25  
151 N Sh Bhekriladze, *Chem Abstr*, 88 (1978) 7707d  
152 N G Gomelauri and S M Kochinova, *Chem Abstr*, 88 (1978) 124409  
153 M D Kurova and O P Bondarenko, *Chem Abstr*, 88 (1978) 124410  
154 V I Karmazin, Z D Roizen and L V Chervanookaya, *Chem Abstr*, 88 (1978) 124411w  
155 V M Khorevich, F I Nagirnyak, A M Komlev and V S Krivonssova, *Chem Abstr*, 88 (1978) 124412x  
156 N A Maletshi, *Chem Abstr*, 88 (1978) 124413y  
157 Yu Se, *Chin Su*, 33 (2) (1981) 37  
158 V M Markova, S P Dashko and I F Bogdanova, *Chem Abstr*, 86 (1977) 458434  
159 S B Kanungo, *Indian J Technol*, 15 (1977) 34  
160 Kh G Purtseladze, E N Soshiashvili, I P Chakhanidze, V A Tskvediani and Kh B Purtseladze, *Chem Abstr*, 83 (1975) 167265r  
161 I P Chakhanidze, N M Chanturiya, E N Bogoyavleuski, B A Dzhnanashvili, T K Chakoniya and I P Oshoridze, *Chem Abstr*, 87 (1977) 71434f  
162 Kh G Purtseladze, *Chem Abstr*, 88 (1978) 77083d  
163 Kh G Purtseladze, *Chem Abstr*, 87 (1977) 56300m  
164 I P Chachanidze, M I Swanidze and I V Raviashvili, *Chem Abstr*, 87 (1977) 56299t.  
165 S B Kanungo and B R Sant, *Australas Inst Min Metall Proc*, 250 (1974) 17  
166 S B Kanungo and B R Sant, *Trans Indian Inst Met*, 27 (1974) 62  
167 S B Kanungo and B R Sant, *Indian Pat*, 128,381 (to Council of Scientific and Industrial Research) (30 Mar 1974)  
168 A P Korobeinikov, I Ya Ivashentsev, N V Tolstoguzov and M L Polyakov, *Izv Vyssh Uchebn Zaved Gorn Zh*, 17(5) (1974) 169  
169 Kh G Purtseladze, E N Shoshiashvili and T A Maslentsova, *Chem Abstr*, 87 (1977) 56301x  
170 Yu M Kartvelishvili and Z M Mirdzhanshvili, *Chem Abstr*, 88 (1978) 77084e  
171 K I Tischenko and B N Bezyazykov, *Chem Abstr*, 88 (1978) 124408a  
172 Ya V Dashavski, A I Ponomarev, M S Sklyarenko and V I Kashin, *Chem Abstr*, 88 (1978) 92839y  
173 I P Rogachev, N A Kravchenko, V V Kasyan, V I Pilipenko and V V Shevchenko, *Chem Abstr*, 86 (1977) 19994z  
174 D V Kurnuskho, N P Lyakishev, V M Ermolov, V T Zubanov and N A Boranov, *Chem Abstr*, 88 (1978) 92887n  
175 R I Agladze, N V Demuriya and D G Bhengelia, *Chem Abstr*, 85 (1976) 146366a

- 176 Ya I Fomin, *Fiz Khim Osn Metall Margantsa (Mater Vses Soveshch) Inst* 1975 (1977) 63
- 177 S B Kanungo and B R Sant, *J Inst Miner Process*, 8 (1981) 359
- 178 J O Hay, cited in R E Kirk and D F Othmer (eds), *Encyclopedia of Chemical Technology*, Vol 8, Wiley, New York, 1952, p 730
- 179 G Almassy *et al*, *Hung Pat*, 155,648 (22 Feb 1969)
- 180 R I Agladze, *Chem Abstr*, 81 (1974) 9737e
- 181 A Manilici, M Guran, G Facsko, I Radoi, A Crisan, A Gotz and P Ilie, *Mine, Pet Gaz*, 26 (1975) 397
- 182 S Djaja and S Purwadaria, *Laporan-Lembaga Metall (Indones)*, 10 (1976) 30
- 183 N V Demurya and R I Agladze, *US Pat*, 3,790,458 (5 Feb 1974)
- 184 J Formanek, J Bawer and F Nekvasil, *Sb Vys Sk Chem Technol Praze, Mineral, G 18* (1977) 97, *Chem Abstr*, 88 (1978) 53300w
- 185 V O Nwoko, *Chem Age India*, 31 (1980) 262
- 186 A B Lele, P J Roychowduri and V Seshadri, *Trans Indian Inst Met*, 33 (1980) 170
- 187 Van Arsdale, *Hydrometallurgy of Base Metals*, McGraw-Hill, London, 1953, p 21
- 188 K N Moorthy and D S Datar, *J Sci Ind Res, Sect B*, 10 (1957) 196
- 189 A A Yousef, M A Arafa and T R Soulos, *Aufbereit-Tech*, 14 (1973) 162
- 190 P N Dzhapandze and N V Kelbakiani, *Zh Prikl Khim (Leningrad)*, 54 (1981) 1969
- 191 N V Kelbakiani and M G Kapanadze, *Soobshch Akad Nauk Gruz SSR*, 103 (1981) 345
- 192 T Kosaka, *Br Pat*, 1,405,038 (26 Jul 1973)
- 193 Kh G Purtseladze, I P Chakhamidze, E A Bogdonov and I V Chakhamidze, *Chem Abstr*, 83 (1975) 34237j
- 194 Kh G Purtseladze *et al*, *Chem Abstr*, 87 (1977) 87097e
- 195 P K Sahoo, P K Jena, S K Bose and S C Sircar, *Trans Am Inst Min Metall Pet Eng*, 268 (1981) 1816
- 196 Bradley Fitch Process in *Thorpe's Dictionary of Applied Chemistry*, Vol III, 4th edn, 1946, p 486
- 197 O P Molchanova, S P Dashko and V M Markova, *Chem Abstr*, 86 (1977) 45842
- 198 V P Astoff, *Ger Offen*, 2,414,125 (9 Oct 1975)
- 199 S C Das, P K Sahov and P K Rao, *Hydrometallurgy*, 8 (1982) 35
- 200 S C Das, P K Sahoo, V M Pandey, P R Das and P K Jena, *J Electrochem Soc India*, 30 (1981) 86
- 201 A P Popova, I M Vulfovich and V M Markova, *Chem Abstr*, 86 (1977) 75324t
- 202 Kh G Purtseladze and Kh B Purtseladze, *Chem Abstr*, 87 (1977) 87111e
- 203 I Tanabe, E Yoshiyama and T Honda, *Jap Pat*, 75 21,995 (26 Jul 1975)
- 204 A J Swinkels, D Scaife, H Peter and J B Lean, *Austr Pat*, 460,527 (14 Jan 1973)
- 205 V E Kosoturov, E A Bambulovich, I F Bogdonova and V M Markova, *Chem Abstr*, 86 (1977) 75327w
- 206 M I Ansari, *Indian J Technol*, 15 (1977) 315
- 207 E S Nossen, *US Pat*, 2,681,268 (15 Jun 1974), *Chem Abstr*, 48 (1954) 13185
- 208 J Y Welsh, *US Pat*, 3,780,158 (18 Dec 1973)
- 209 J Y Welsh, *US Pat*, 3,780,159 (18 Dec 1973)
- 210 Diamond Shamrock Corp, *Neth Pat*, 73,14,968 (2 May 1975)
- 211 Diamond Shamrock Corp, *Fr Pat Appl*, 2,249,037 (23 May 1975)
- 212 J Y Welsh, *Ital Pat*, 63988 (17 Apr 1978)
- 213 N Maekawa, *Jpn Kokai*, 78 82,697 (29 Jul 1978)
- 214 J P Brenet and L Pons, *Fr Pat*, 907,1443 (1966)
- 215 C R Talpade and P G Pradhan, *Indian Chem Manuf*, 13 (10) (1975) 11
- 216 C R Talpade, S M Donde and P G Pradhan, *Chem Era* 12(8) (1976) 317
- 217 J P Brenet, *CR Acad Sci*, 243 (1956) 424

- 218 H Tamura, in S Yoshizawa *et al* (eds), *Electrochemistry of Manganese Dioxide and Manganese Dioxide Batteries in Japan*, Vol 2, U S Branch Office, Electrochem Soc Jpn, Cleveland, OH, 1973, p 189
- 219 C R Talpade and P G Pradhan, *Indian Chem Manuf*, 15(9) (1977) 11
- 220 S Gosh and P G Pradhan, *SAEST Trans*, 11 (1976) 353
- 221 L Balewski, J Brenet and G Coeffier, *C R Acad Sci*, (1966) 172
- 222 H Hess and L Carius, *Mellor*, 12 (1932) 255
- 223 J P Brenet *et al*, *C R Acad Sci*, 259 (1964) 814, 1226
- 224 Cited in A Kozawa and R J Brodd (eds), *MnO<sub>2</sub> Symp Proc*, Cleveland, OH, 1 (1975), *Ger Pat*, 709,475 (to Leclanché S A), 711,102 (to Leclanché S A), 630,024 (to I G Farenindustrie, A G)
- 225 C F Burgess, *US Pat*, 1,305,250, 1,305,251 and 1,305,252 (to Burgess Battery Co) (3 Jun 1919)
- 226 C Rosetti, *US Pat*, 2,186,929 (to Leclanché S A) (9 Jun 1941)
- 227 W Mütter, *Ger Pat*, 879,387 (to Farben Fabrikent, Bayer A G) (11 Jun 1953)
- 228 G Fukuda *et al*, *Jpn Pat*, 775 (5 Sep 1956)
- 229 O F Creanga, *Rev Chim*, 8 (1957) 251
- 230 R V Landquist, *US Bureau of Mines, Departmental Investigation No 5357*, (1957) p 34
- 231 R L Sastry, *Electro-Technol (India)*, 3 (1959) 16
- 232 C S Rao, *J Electrochem Soc India*, 15 (1966) 105
- 233 M Anayama, S Kasori and K Takahashi, *Denki Kagaku*, 33 (1965) 371
- 234 Yuzuyama, M Anayama, S Kasori and K Takahashi, *Denki Kagaku*, 34 (1966) 962
- 235 Y Uetani, T Iwamura and Y Ishikawa, *MnO<sub>2</sub> Symp Proc*, Tokyo, 2 (1980) 11
- 236 S Komiya, *Prog Batteries Sol Cells*, 4 (1982) 149
- 237 V M Burns and R G Burns, *MnO<sub>2</sub> Symp Proc*, Cleveland, OH, 1 (1975) 288
- 238 V M Burns and R G Burns, *MnO<sub>2</sub> Symp Proc*, Cleveland, OH, 1 (1975) 306
- 239 V Ettel and J Veprek-Siska, *Chem Listy*, 57 (1963) 785
- 240 M Fleischer and W E Richmond, *Econ Geol*, 38 (1943) 269
- 241 J Brenet and A Héraud, *C R Acad Sci*, 228 (1948) 1487
- 242 J A Tauber, *X-Ray Diffraction Key to Manganese Oxide Minerals*, E J Lavino, Philadelphia, 1964
- 243 W F Nye, S B Levin and H H Kedesdy, *Proc 13th Annual Power Sources Conf*, Atlantic City, NJ, 1959, p 125
- 244 M Voinov, *Electrochim Acta*, 27 (1982) 833
- 245 R G Burns and V M Burns, in G P Glashby (ed), *Marine Manganese Deposits*, 1977, p 195
- 246 A St John, *Phys Rev*, 21 (1923) 389
- 247 A Ferrari, *Atti Accad Naz Lincei Rend*, 3 (1926) 224, *Chem Abstr*, 20 (1926) 20
- 248 G M Clark, *The Structure of Non-Molecular Solids*, Appl Sci, Barking, U K, 1972
- 249 P M de Wolff, *Acta Crystallogr*, 12 (1959) 341
- 250 R G Burns and V M Burns, *MnO<sub>2</sub> Symp Proc*, Tokyo, 2 (1980) 97
- 251 P M de Wolff, J W Visser, R Giovanoli and R Brutsch, *Chimia*, 32 (1978) 257
- 252 R Giovanoli, in I M Varentsov and G Y Graselli (eds), *Geology and Geochemistry of Mn Nodules*, Vol 1, Hungarian Academy of Sciences, 1980
- 253 E Preisler, *J Appl Electrochem*, 6 (1976) 311
- 254 F Freund, E Konen and E Preisler, *MnO<sub>2</sub> Symp Proc*, Cleveland, OH, 1 (1975) 328
- 255 K M Parida, S B Kanungo and B R Sant, *Electrochim Acta*, 26 (1981) 435
- 256 R Giovanoli, *MnO<sub>2</sub> Symp Proc*, Tokyo, 2 (1980) 113 - 133
- 257 R Giovanoli, *Prog Batteries Sol Cells*, 2 (1979) 118
- 258 J P Gabano, B Morignat, E Fialdes, B Emery and J F Laurent, *Z Phys Chem*, 46 (1965) 359

- 259 H Ikeda, T Saito and H Tamura, *MnO<sub>2</sub> Symp Proc, Cleveland, OH, 1* (1975) 384
- 260 B Schumm *et al* (eds), *MnO<sub>2</sub> Symp Proc, Tokyo, 2* (1980) 599 (appendix)
- 261 A Kozawa and R J Brodd (eds), *MnO<sub>2</sub> Symp Proc, Cleveland, OH, 1* (1975) 497
- 262 S Turner and P R Buseck, *Science*, 203 (1979) 456
- 263 R Giovanoli, R Maurer and W Feitknecht, *Helv Chim Acta*, 50 (1967) 1 - 9
- 264 R G Burns, K Matsuiki and A Kozawa, *MnO<sub>2</sub> Symp Proc, Tokyo, 2* (1980) 683
- 265 A Bystrom and A M Bystrom, *Acta Crystallogr*, 3 (1950) 194, 4 (1951) 469
- 266 G Butler and H R Thirsk, *Acta Crystallogr*, 5 (1952) 288
- 267 N Yamamoto *et al*, *Jpn J Appl Phys*, 13 (1974) 723
- 268 W Richmond and M Fleischer, *Am Mineral*, 27 (1942)
- 269 H F McMurdie, *Trans Electrochem Soc*, 86 (1944) 12
- 270 J Brenet, *Bull Soc Fr Minéral Cristallogr*, 77 (1954) 797
- 271 G Butler and H R Thirsk, *Acta Crystallogr*, 3 (1950) 146
- 272 A D Wadsley, *Acta Crystallogr*, 6 (1953) 433
- 273 P H Delano, *Ind Eng Chem*, 42 (1950) 523
- 274 K H Marwell, G Butler and H R Thirsk, *J Chem Soc*, (1952) 4210
- 275 C Mitsusada *et al*, *Kagoshima Daigaku Kogakubu Kenkyu Hokoku*, 22 (1980) 125 - 131
- 276 J E Post, R B Von Drele and P R Buseck, *Acta Crystallogr, Sect B*, 38 (1982) 1056 - 1065
- 277 L A Bursill and G Grzanic, *Acta Crystallogr, Sect B*, 36 (1980) 2902 - 2913
- 278 W Feitknecht and W Marti, *Helv Chim Acta*, 28 (1945) 129, 149
- 279 A D Wadsley, *J Am Chem Soc*, 72 (1950) 1781
- 280 W Buser, P Graf and W Feitknecht, *Helv Chim Acta*, 38 (1955) 810
- 281 O Bricker, *Am Mineral*, 50 (1965) 1246
- 282 R Giovanoli, *Chimia*, 23 (1969) 470
- 283 R Giovanoli and E Staehli, *Chimia*, 24 (1970) 49
- 284 R Giovanoli, E Staehli and W Feitknecht, *Helv Chim Acta*, 53 (1970) 209 - 2, 453 - 464
- 285 R Giovanoli, H Buhler and K Sokolowska, *J Microsc (Paris)*, 18 (1973) 271 - 284
- 286 R Giovanoli and R Brutsch, *Chimia*, 33 (1979) 372
- 287 G Arrhénius *et al*, in C Lalou (ed), *La Genèse des Nodules de Manganèse*, Colloq Intern Centre National de la Recherche Scientifique, *C R Acad Sci*, 289 (1979) 410
- 288 S Crane, *Ph D Thesis*, Scripps Institute of Oceanography, La Jolla, CA, 1979
- 289 C Delmas and C Fouassier, *Z Anorg Allg Chem*, 420 (1970) 184 - 192
- 290 L S Dent Glasser and L Ingram, *Acta Crystallogr, Sect B*, 24 (1968) 1233 - 1236