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The behaviour of MnO_2 in strongly acidic solutions

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Different MnO_2 samples were equilibrated with H_2SO_4 solutions of varying concentrations and the equilibrium concentration of dissolved Mn^{3+} determined experimentally. Leaching in strong acid appears to be a useful tool for characterizing different types of MnO_2 materials. The equilibrium concentration of dissolved Mn^{3+} showed a sharp drop above 9 M H_2SO_4. The crystal structure of MnO_2 was not affected by acid leaching and only a slight grain coarsening was observed.

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1. Dissolution chemistry

The electrochemical processes of MnO_2 in strongly acidic solutions involve a number of soluble manganese species [1, 2] of different valency, namely, Mn(II), Mn(III), Mn(IV) and Mn(VII). These soluble species may be distinguished by their absorption spectra and their equilibria have been studied by absorption spectrophotometry [3, 4]. For

$$2Mn^{3+} \rightleftarrows Mn^{2+} + Mn^{4+}$$

values for the formal equilibrium constant

$$K = [Mn^{2+}] \cdot [Mn^{4+}]/[Mn^{3+}]^2$$

of 4.8×10^{-2} in 4 mol dm^{-3} H_2SO_4 to 2.0×10^{-3} in 12 mol dm^{-3} H_2SO_4 have been reported [5]. Clearly, Mn^{3+} is the dominant higher valency species. It is characterized by a dark, red-violet colour. Both Mn^{3+} and Mn^{4+} are relatively stable with respect to the oxidation of water (oxygen evolution); their half-lives at room temperature in 6 mol dm^{-3} H_2SO_4 were found to be about two and six months respectively [3]. The permanganate ion, Mn(VII), on the other hand, is quite unstable and decomposes with evolution of oxygen to Mn^{3+} within hours.

2. Electrochemical equilibria between dissolved species and MnO_2

Electrochemical equilibria may be expressed formally in terms of pH–potential relationships [6, 7].

$$Mn^{2+} \rightleftarrows Mn^{3+} + e^- \qquad (1)$$

$$E = 1.509 + 0.0591 \log [Mn^{3+}] - 0.0591 \log [Mn^{2+}]$$

and

$$Mn^{3+} \rightleftarrows Mn^{4+} + e^- \qquad (2)$$

$$E = 1.630 + 0.0591 \log [Mn^{4+}] - 0.0591 \log [Mn^{3+}].$$

For the equilibria with solid MnO_2 one formally has:

$$Mn^{2+} + 2H_2O \rightleftarrows MnO_2 + 4H^+ + 2e^- \qquad (3)$$

$$E = 1.228 - 0.1182\,pH - 0.0295 \log [Mn^{2+}],$$

$$Mn^{3+} + 2H_2O \rightleftarrows MnO_2 + 4H^+ + e^- \qquad (4)$$

$$E = 0.948 - 0.2364\,pH - 0.0591 \log [Mn^{3+}]$$

and

$$Mn^{4+} + 2H_2O \rightleftarrows MnO_2 + 4H^+ \qquad (5)$$

from which the following formal *equilibrium 'activities' for higher valent manganese species* are derived:

$$\log [Mn^{3+}] = -4.75 + 0.5 \log [Mn^{2+}] - 2\,pH \qquad (6)$$

and

$$\log [Mn^{4+}] = -11.5 - 4\,pH. \qquad (7)$$

The formation of Mn^{3+} by reaction between Mn^{2+}

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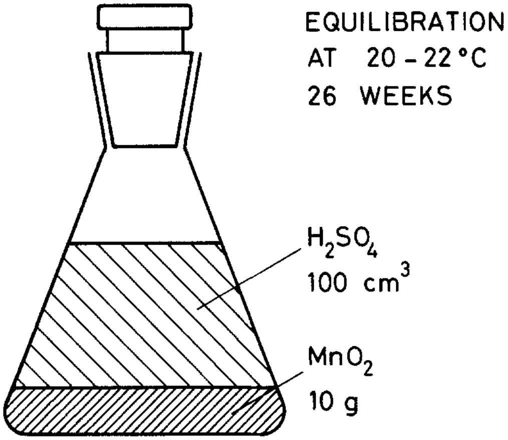

Fig. 1. Equilibration conditions for MnO_2 in H_2SO_4 solutions.

and MnO_2 may be visualized either as a combination of the forward reaction of the process in Equation 1 with the back reaction of Equation 4, or by the combination of twice the back reaction of Equation 4 with the forward reaction of 3, resulting, in either case, in

$$MnO_2 + Mn^{2+} + 4H^+ \rightarrow 2Mn^{3+} + 2H_2O. \quad (8)$$

Mn^{3+} is the first oxidation product of Mn^{2+} and appears to play a key role as intermediate in the electrolytic process for manufacturing MnO_2 [8–10]. Its 'disproportionation' into Mn^{2+} and MnO_2, the reverse of Equation 8, involves the electrochemical component reactions already mentioned but in the opposite directions.

In strongly acid solutions, and depending also on the Mn^{2+} concentration, the electrode potential of MnO_2 rises above that of the oxidation of water to oxygen. Under these conditions MnO_2 should decompose theoretically according to

$$2MnO_2 + 6H^+ \rightarrow 2Mn^{3+} + 3H_2O + \tfrac{1}{2}O_2 \quad (9a)$$

or

$$MnO_2 + 2H^+ \rightarrow Mn^{2+} + H_2O + \tfrac{1}{2}O_2. \quad (9b)$$

The rate of this process, however, appears to be inhibited because of an oxygen overvoltage.

3. Non-stoichiometry of MnO_2

It is well known that Equations 3 and 4 represent the actual processes inaccurately. In fact, one has to take into account that MnO_2 has a variable stoichiometry [11]. When MnO_2 is equilibrated with strong acids one should expect trivalent manganese to be leached from the lattice [1]. This may be formulated as follows:

$$\begin{aligned}&(MnO_2)_{2n-3}\cdot(MnOOH)_{4-2n}\cdot mH_2O\\ &+3(4-2n)H^+ \rightarrow (2n-3)MnO_2\\ &+(4-2n)Mn^{3+}+(8-4n+m)H_2O. \quad (10)\end{aligned}$$

4. Experimental procedure

Samples (10 g) of commercial electrolytic γ-MnO_2 (Toya Soda Manufacturing Co., type HH, ICS No. 1) were treated with H_2SO_4 solutions (100 cm^3) of different concentrations over a

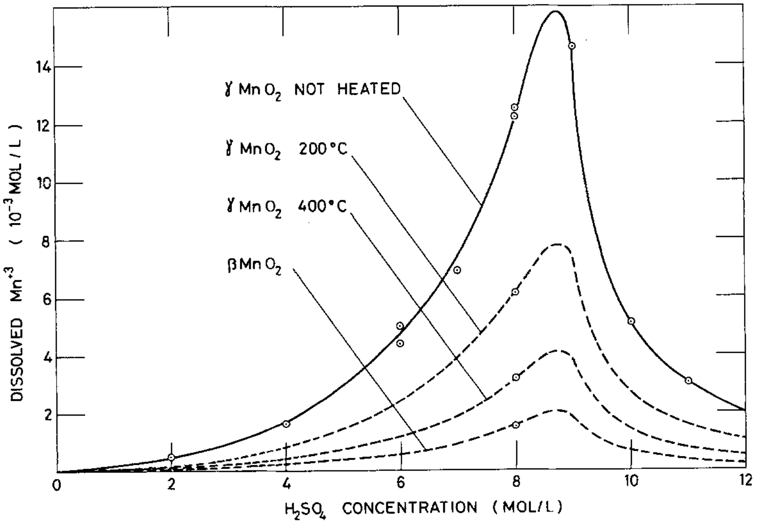

Fig. 2. Equilibrium concentrations of Mn^{3+} as a function of H_2SO_4 concentration.

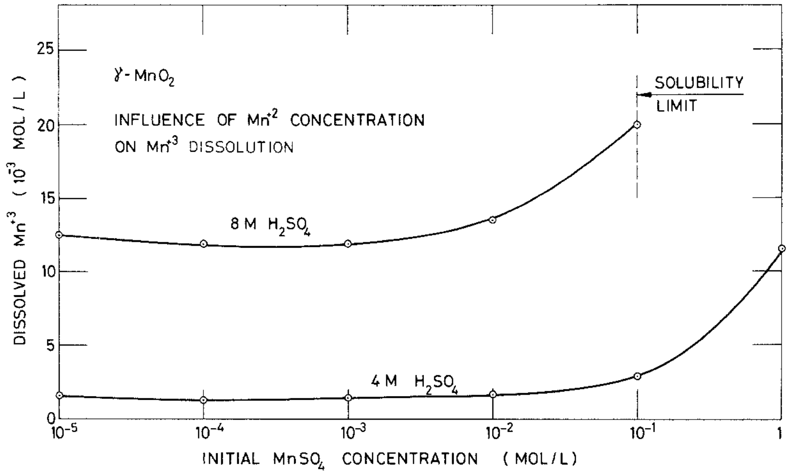

Fig. 3. Influence of $MnSO_4$ concentration on Mn^{3+} dissolution.

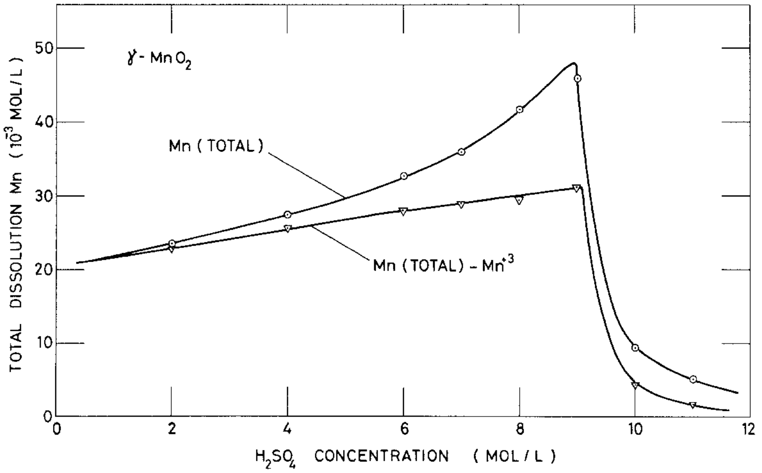

Fig. 4. Total amount of dissolved manganese (Mn^{2+} plus Mn^{3+}).

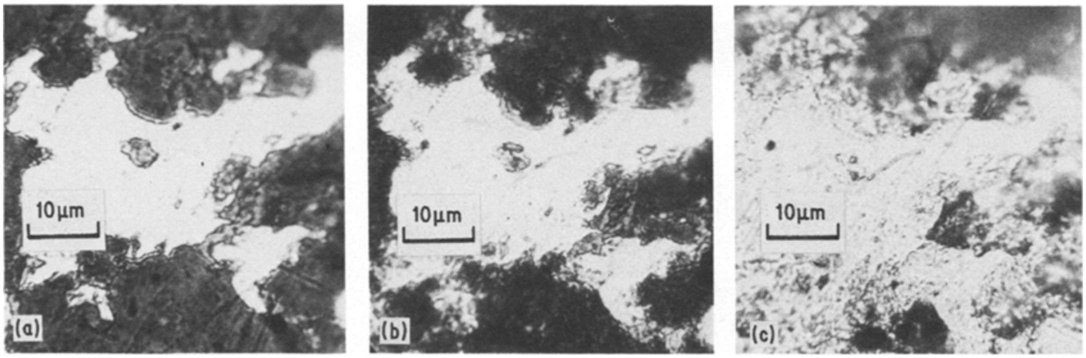

Fig. 5. Dissolution of γ-MnO_2 particles (dark portions) in 4 mol dm^{-3} H_2SO_4. (a) 0 h, (b) 6 h and (c) 96 h.

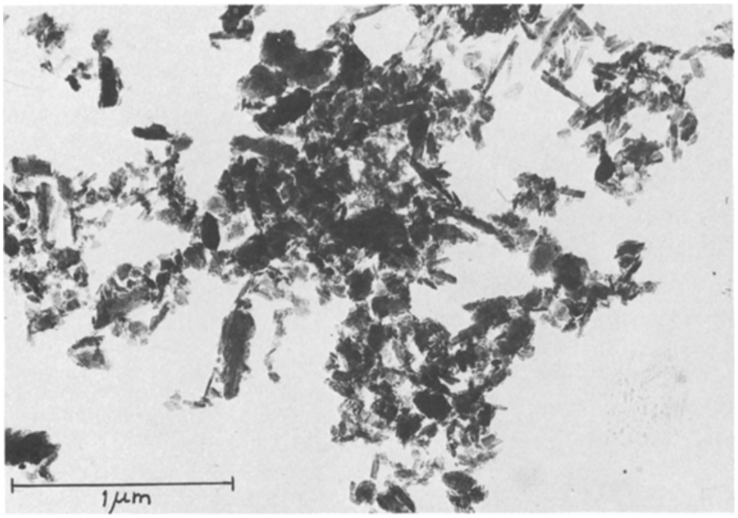

Fig. 6. Electron micrograph of the starting material γ-MnO_2, ICS No. 1, at × 50 000 prior to acid treatment.

period of 26 weeks in glass-stoppered Erlenmeyer flasks at room temperature (21 ± 1° C). The flasks were shaken for a few minutes once per week (Fig. 1). At the end of the equilibration period, the supernatant solution was carefully pipetted off and analysed. In analysing the solution for Mn^{3+}, a 10 cm^3 sample was mixed with 10 cm^3 of 0.01 mol dm^{-3} $FeSO_4$ and the excess $FeSO_4$ was back titrated with 0.01 mol dm^{-3} $KMnO_4$. Total manganese in solution was determined by complexometric titration. The equilibration tests were also carried out with heat-treated γ-MnO_2 (24 h in air at 200 and 400° C). The behaviour of well crystallized β-MnO_2, produced by thermal decomposition of a concentrated $Mn(NO_3)_2$ solution, was also investigated. Electron micrographs and X-ray diffraction patterns were taken before and after the acid treatments.

5. Results

The concentration of dissolved Mn^{3+}, in equilibrium with MnO_2, was found to increase strongly with H_2SO_4 concentration (Fig. 2), which is in qualitative agreement with Equation 6. However, the measured values are much higher than predicted from Equation 6, which indicates that most of the $[Mn^{3+}]$ (in particular for the case of un-

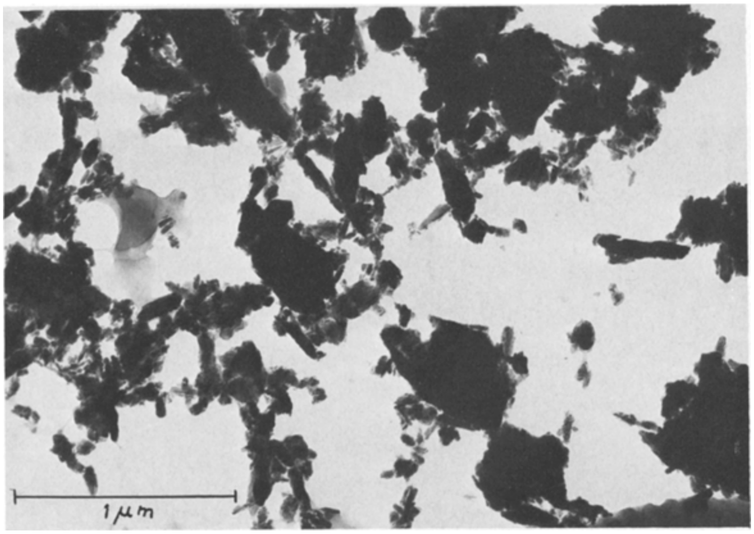

Fig. 7. Electron micrograph of γ-MnO_2 ICS No. 1, after 26 weeks equilibration in 2 mol dm^{-3} H_2SO_4.

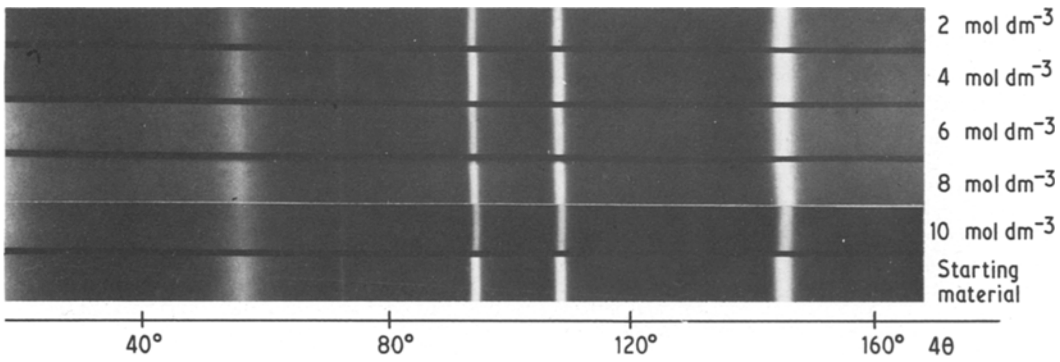

Fig. 8. X-ray diffraction pattern (FeKα) of γ-MnO_2 treated for 6 months in H_2SO_4.

treated γ-MnO_2) stems from the leaching process [10]. Surprisingly, the concentration of dissolved Mn^{3+} dropped abruptly above 9 mol dm^{-3} H_2SO_4, probably as a result of 'salting-out' effects. Fig. 2 also demonstrates that much less Mn^{3+} is released into solution when the samples are heat-treated in air. The least amount of Mn^{3+} was found with β-MnO_2 produced by pyrolysis of $Mn(NO_3)_2$. *Leaching in acid is thus a useful tool for characterizing different types of* MnO_2 and could, with proper consideration of the degree of oxidation, possibly correlate with 'battery activity'. When $MnSO_4$ is added in varying amounts to the H_2SO_4 leach solutions (Fig. 3), dissolved Mn^{3+} stayed constant up to about 10^{-2} mol dm^{-3} $MnSO_4$, and then increased, in qualitative agreement with Equation 6. It would appear that the γ-MnO_2 samples already initially contained sufficient Mn^{2+}, probably in the form of occluded or surface-adsorbed $MnSO_4$ stemming from the manufacturing process, to produce that level of Mn^{2+} in solution. It represents about 1 to 2% of the total manganese in the sample. Fig. 4 shows the total amount of manganese, Mn(II) and Mn(III), present in solution, as determined by complexometric titration, for the case of untreated γ-MnO_2. Subtracting the values of Mn^{3+} from Fig. 2, one obtains a measure of the dissolved Mn^{2+}. This curve also shows a sharp drop above 9 mol dm^{-3} H_2SO_4.

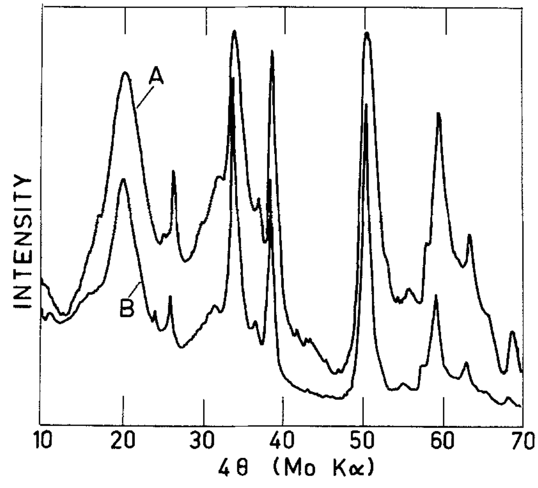

Fig. 9. Densitometer curves for γ-MnO_2 before (curve A) and after (curve B) treatment in 10 mol dm^{-3} H_2SO_4 for 26 weeks.

Table 1 lists the maximum total amount of dissolved Mn^{2+} and Mn^{3+} (in 8 mol dm^{-3} H_2SO_4), expressed as a percentage of the total manganese in the sample.

At least a small portion of the dissolved Mn^{2+} (and Mn^{3+}) must stem from the thermodynamically required dissolution of MnO_2 in strong acids according to Equation 9 and some Mn^{3+} must stem from the equilibration process of Equation 8. Chemical dissolution of entire MnO_2 grains is indeed observed, for example, in 4 mol dm^{-3} H_2SO_4 and is shown in Fig. 5. These photographs show MnO_2 particles (dark portions), pressed onto a very fine platinum screen (wire diameter 0.08 mm),

Table 1. Amount of dissolved Mn^{2+} and Mn^{3+} in 8 mol dm^{-3} H_2SO_4 expressed as a percentage of the total Mn in the sample

Sample	*Mn^{2+}*	*Mn^{3+}*
γ-MnO_2	2.71	1.06
γ-MnO_2 (200° C)	1.79	0.54
γ-MnO_2 (400° C)	1.24	0.28
β-MnO_2	0.95	0.13

forming the white background in the pictures, at × 1500 magnification. The experimental technique for observing ultrathin MnO_2 electrodes *in situ* has been described previously [2].

Electron micrographs of γ-MnO_2 samples, taken before and after the 26 week acid treatment, reveal a slight grain coarsening (Figs. 6 and 7). Also, the X-ray diffraction patterns show slightly less broadened lines after the treatment, particularly at the higher acid concentrations (Fig. 8). Acid treated samples, however, still exhibit an unchanged, typical γ-MnO_2 structure (Fig. 9).

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