

Chemical and phase composition of manganese oxides obtained by Mn(II) oxidation in nitrate solutions

Ye.V. Kuz'minskii, A.A. Andriiko, L.I. Nyrkova

*Scientific Engineering Center 'Tekhnoelektrokhim', Institute of General and Inorganic Chemistry, Ukrainian Academy of Sciences,
32/34 Prospect Palladina, 252680 Kiev-142, Ukraine*

Received 25 November 1993; in revised form 18 April 1994; accepted 23 April 1994

Abstract

Chemical and phase composition of manganese oxides obtained by Mn(II) oxidation in nitrate solutions has been studied by the methods of differential thermal analysis, IR spectroscopy, X-ray phase and chemical analyses. The product of Mn(II) oxidation with nitrate has been shown to be a partially hydrated oxide of the MnO_{2-n} composition, $0.2 < n < 0.4$. It has been found that the average degree of oxidation of manganese is affected by conditions of the synthesis: it increases with decreasing nitrate concentration and temperature. Treatment of the product with diluted nitric acid leads to a disproportionation of underoxidized Mn(III) compounds into Mn(II) and Mn(IV). The final product is γ - MnO_2 .

Keywords Manganese oxides; Chemical composition; Phase composition

1. Introduction

Synthetic manganese dioxide used in the batteries and other fields of engineering is most frequently produced by oxidation of compounds of bivalent manganese. The oxidizers may be bromine, ammonium persulfate, hydrogen peroxide [1], electric current [2], etc. In particular, the process of Mn(II) oxidation with nitrate in thermal decomposition of manganese nitrate within the range of 200 to 300 °C is commonly used in order to obtain β - MnO_2 (synthetic pyrolusite) [3].

It has been established in our previous work [4] that the oxidation of Mn(II) with nitrate, ions are occurring in aqueous solutions at pH varying from 6.5 to 7.8.

The reaction rate is of an order of zero for Mn^{2+} , but more than one for nitrate, and it depends on the pH in a complicated manner. The kinetic regularities are described in terms of a mechanism involving pre-hydrolysis with the formation of colloidal particles and their subsequent oxidation with NO_3^- ions. The reaction product is a dark brown precipitate — a mixture of hydrated oxides MnO_{2-n} . In the present work, the phase and chemical composition of these oxides has been studied, as well as their interaction with solutions of nitric acid.

2. Experimental

Reactants for this study were prepared in the following way. The oxidation of Mn(II) was carried out in a solution of manganese nitrate with a concentration of 1 M/l at pH is 7. To keep the pH constant, a solution of 5 N NaOH was added step by step, as the initial solution became acidified by 0.1 to 0.2 pH units. After manganese had been precipitated, the precipitate was filtered, rinsed with water, air dried at either room temperature or at 100 °C and then the total manganese has been analysed by the complexometric method [5]; the content of active MnO_2 has been analysed by reduction with oxalic acid and subsequent titration of the excess of $H_2C_2O_4$ with potassium permanganate [6]. The content of oxygen per one manganese atom was calculated from the results of the chemical analysis. The content of sodium in the precipitates was determined by means of flame photometric analysis. The results obtained are presented in Table 1.

The samples produced were investigated by X-ray phase analysis, IR spectroscopy and differential thermal analysis. Diffractograms of the samples were taken at the DRON-3M diffractometer (Cu $K\alpha$ radiation). IR spectra of the samples pressed as tablets with KBr were recorded with the Specord spectrophotometer. Thermograms were taken under the following conditions: atmosphere: air, crucible: platinum, weight. 250

Table 1
Conditions of synthesis and composition of samples

| Sample numbers | Conditions of synthesis | | | Composition (wt.%) | | | Empirical formula $MnO_{y_1(y)}$ | Sample moisture (wt.%) |
|----------------|--|---|---------------------------|--------------------|---------|---------|----------------------------------|------------------------|
| | Temperature (°C) | NO_3^-/Mn^{2+} ratio, $C_{Mn^{2+}} = 1$ mol/l | Time of precipitation (h) | Mn_2O_3 | MnO_2 | Na_2O | | |
| 1 | 50 | 2 | 35 | 60.4 | 37.3 | 0.06 | 1.68 | 1.88 |
| 2 | 25 | 3 | 51 | 61.4 | 38.8 | 0.12 | 1.68 | 1.09 |
| 3 | 50 | 3 | 45 | 79.5 | 16.3 | 0.036 | 1.58 | 0.73 |
| 4 | 25 | 2 | 56 | 44.6 | 57.6 | 0.38 | 1.77 | 1.35 |
| 5 | Samples 1 to 4 treated with HNO_3 solution at room temperature | | | 57.8 | 43.9 | 0.047 | 1.70 | 0.67 |
| 6 | | | | 42.2 | 60.0 | 0.058 | 1.78 | 5.33 |
| 7 | | | | 68.7 | 31.9 | 0.038 | 1.65 | 2.15 |
| 8 | | | | 51.5 | 50.9 | 0.15 | 1.74 | 3.03 |
| 9 | Samples 1 to 4 boiled with diluted HNO_3 | | | 1.8 | 97.0 | 0.04 | $\gamma-MnO_2$ | 2.15 |

to 350 mg, and heating rate: 5 °C/min. Discharge curves of samples were measured in a flat coin-type lithium cells (diameter: 23 mm, thickness: 2.5 mm) under loading 5.6 k Ω .

3. Results and discussion

The product precipitated from the $Mn(NO_3)_2$ solution is partially hydrated oxide with an intermediate stoichiometry (between Mn_2O_3 and MnO_2). The data obtained show that the average degree of oxidation of manganese depends on the synthesis conditions: it increases with decreasing NO_3^- concentration and temperature. Since the decrease of the above parameters lowers the rate of the process [4], it can be concluded that the degree of manganese oxidation depends inversely on the rate of the precipitation of the product.

Whatever the conditions of the precipitation, the nature of diffractograms of the samples is identical (Table 2). For samples dried at room temperature, the presence of the $MnOOH$ (manganite) and Mn_2O_3 oxide (α -kurnakite [1] or $\gamma-Mn_2O_3$ according to the nomenclature recently accepted [7]) phases has been revealed. Also, there are a few weak reflexes which may be attributed to hydrated polymanganites of type $(Na, Mn)O_2 \cdot nMnO_2 \cdot xH_2O$ [1]. After drying the samples at 100 °C, only the lines of $\gamma-Mn_2O_3$ remain (column 3, Table 2). Nevertheless, the product obtained is not a single-phase one, which is verified by the data of thermal analysis. A typical derivatogram of the sample shown in Fig. 1 (curve 1) has the following characteristic regions: (i) the loss of fixed water at 145 to 370 °C; (ii) oxidation at 395 to 470 °C, which is characteristic of the $\gamma-Mn_2O_3 \rightarrow \beta-MnO_2$ conversion [1]; (iii) decomposition $\beta-MnO_2 \rightarrow \beta-Mn_2O_3$, which starts at 559 to 595 °C; (iv) oxidation at 600 to 700 °C, and (v) thermal

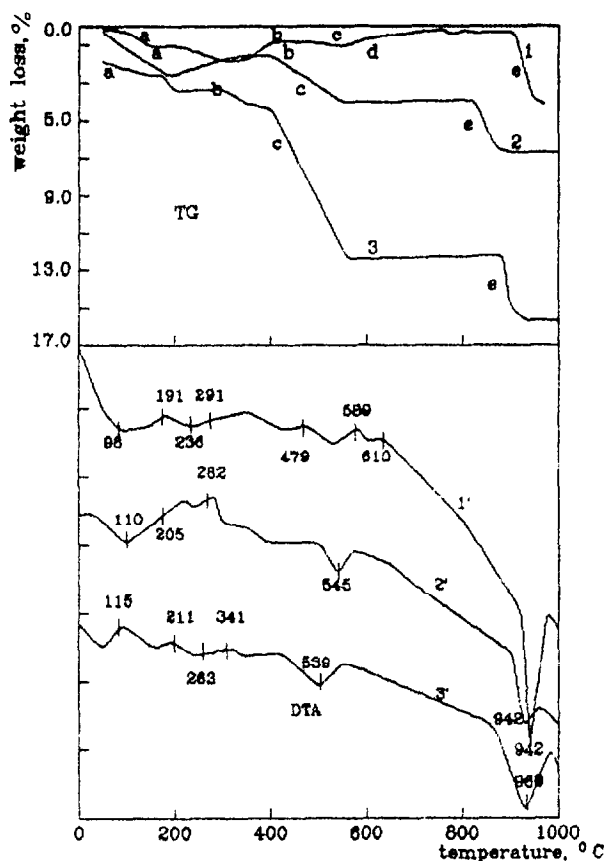


Fig. 1. Thermograms of samples 4, 8 and 9, see Table 1 (curve 1, 1', 2, 2' and 3, 3', respectively).

decomposition at 960 to 990 °C, characteristic of the $\beta-Mn_2O_3 \rightarrow Mn_3O_4$ (hausmannite). Stages (iii) and (iv) are overlapping partly.

Treatment of the product with diluted nitric acid at room temperature (samples 5 to 8, Table 1) leads to the disappearance of stage (iv) in the derivatograms (curve 2, Fig. 1). In this case the oxygen-to-manganese

Table 2
Results of X-ray phase analysis of precipitates

| Number analysis | Samples 1 to 4 (Table 1) | | Sample 1 dried at 100 °C | | Sample 9 (Table 1) | | γ -Mn ₂ O ₃ [8] | | MnOOH [9] | | γ -MnO ₂ [10] | |
|-----------------|--------------------------|-------|--------------------------|-------|--------------------|-------|--|-------|-----------|-------|---------------------------------|-------|
| | d (Å) | I (%) | d (Å) | I (%) | d (Å) | I (%) | d (Å) | I (%) | d (Å) | I (%) | d (Å) | I (%) |
| 1 | 7.37 | 5 | | | | | | | | | | |
| 2 | 6.02 | 5 | | | | | | | | | | |
| 3 | 5.44 | 4 | | | | | 4.93 | 40 | | | | |
| 4 | 4.89 | 22 | 4.90 | 23 | | | | | | | | |
| 5 | 4.80 | 7 | | | 3.95 | 80 | | | | | 3.96 | 100 |
| 6 | 4.02 | 5 | | | | | | | | | | |
| 7 | 3.68 | 6 | | | | | | | | | | |
| 8 | 3.48 | 7 | | | | | | | | | | |
| 9 | 3.39 | 70 | | | | | | | 3.40 | 100 | | |
| 10 | 3.07 | 32 | 3.07 | 38 | | | 3.08 | 60 | | | 3.07-3.20 | 20 |
| 11 | 2.88 | 7 | | | | | | | | | | |
| 12 | 2.87 | 15 | 2.87 | 14 | | | | | | | | |
| 13 | 2.84 | 15 | | | | | | | | | | |
| 14 | 2.75 | 70 | 2.76 | 78 | | | | | | | | |
| 15 | 2.63 | 18 | | | | | 2.64 | 70 | | | 2.60 | 60 |
| 16 | 2.51 | 16 | | | 2.56 | 10 | | | 2.63 | 60 | | |
| 17 | 2.48 | 100 | 2.48 | 100 | 2.417 | 95 | 2.48 | 100 | 2.53 | 40 | 2.42 | 100 |
| 18 | 2.404 | 30 | | | 2.332 | 30 | | | 2.41 | 80 | | |
| 19 | 2.350 | 15 | 2.321 | 20 | | | 2.39 | 40 | | | 2.32 | 80 |
| 20 | 2.265 | 10 | | | | | | | 2.26 | 60 | | |
| 21 | 2.186 | 12 | | | | | | | | | 2.12 | 80 |
| 22 | 2.032 | 22 | 2.032 | 23 | 2.117 | 56 | 2.03 | 20 | | | 2.05 | 40 |
| 23 | 1.816 | 7 | 1.824 | 7 | | | 1.83 | 30 | | | | |
| 24 | 1.787 | 30 | 1.791 | 22 | | | 1.79 | 20 | | | | |
| 25 | 1.744 | 25 | | | | | | | | | | |
| 26 | 1.695 | 15 | 1.695 | 10 | | | | | | | | |
| 27 | 1.667 | 30 | | | | | | | 1.77 | 80 | | |
| 28 | 1.663 | 10 | | | | | | | 1.71 | 40 | | |
| 29 | 1.573 | 25 | 1.573 | 28 | 1.629 | 100 | 1.59 | 30 | | | 1.637 | 80 |
| 30 | 1.539 | 50 | 1.539 | 50 | | | 1.55 | 60 | | | 1.605 | 60 |
| 31 | 1.497 | 9 | | | | | | | | | | |
| 32 | 1.467 | 3 | 1.465 | 2 | 1.475 | 14 | | | 1.50 | 40 | | |
| 33 | 1.437 | 25 | 1.437 | 18 | 1.421 | 18 | | | 1.44 | 40 | 1.486 | 10 |
| 34 | 1.379 | 5 | 1.379 | 4 | 1.367 | 18 | | | | | 1.422 | 60 |
| 35 | 1.346 | 5 | 1.344 | 4 | | | | | | | 1.362 | 40 |
| 36 | 1.319 | 7 | | | 1.301 | 8 | | | | | | |
| 37 | 1.277 | 7 | 1.274 | 9 | 1.209 | 5 | | | | | 1.306 | 10 |

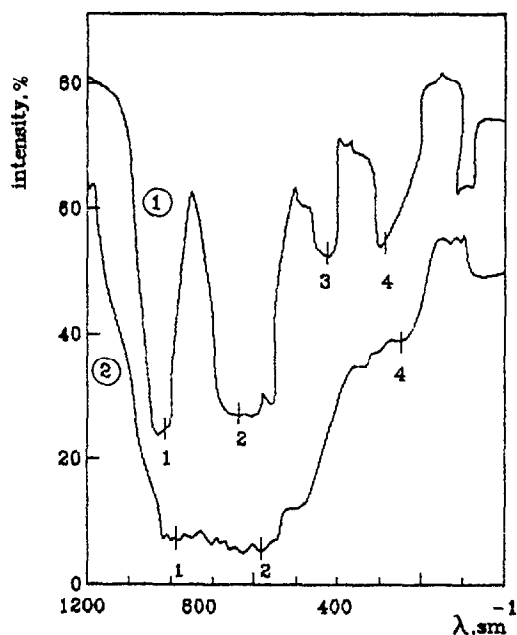


Fig. 2. Infrared adsorption spectra of samples 2 and 6; see Table 1 (curves 1 and 2, respectively).

ratio slightly increases, and qualitative character of diffractograms does not change. This allows one to conclude that process (iv) is the oxidation of bivalent manganese which seems to be present as X-ray amorphous polymanganites of the $\text{MnO}_n \cdot \text{MnO}_2$ type [1] or partly in the form of Mn_3O_4 , whose diffractogram is very similar to that of $\gamma\text{-Mn}_2\text{O}_3$.

Boiling the samples in diluted nitric acid for a short period (up to 30 min) results in the formation of a single product – $\gamma\text{-MnO}_2$ – which is verified by chemical, X-ray phase (Table 2) and thermal (Fig. 1, curve 3) analysis.

A high degree of conversion in this case is seen in IR spectra (Fig. 2). The spectra of the samples 1 to 8, presented in Table 1, are the same (curve 1) and have four rather narrow absorption bands at 1050, 980, 640 and 500 cm^{-1} which is likely to occur due to the presence of Mn ions with different valences. After the samples have been boiled in diluted nitric acid, bands 1 and 2 merge into a wide band, the absorption band 3 disappears and a shoulder appears instead of band 4. Spectrum 2 (Fig. 2) is characteristic of the preparations of synthetic MnO_2 [11].

4. Conclusions

The results obtained allow the following conclusions to be drawn.

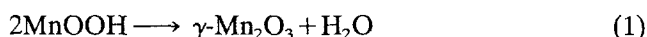
1. The product of Mn(II) oxidation with aqueous nitrate solution is a mixture of partially hydrated manganese oxides of the composition MnO_{2-n} , $0.2 < n < 0.4$. The higher the oxygen-to-manganese ratio, the lower

the rate of oxidation (temperature and NO_3^- concentration in the solution).

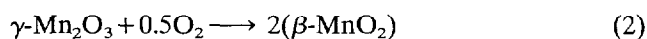
2. The product includes compounds of Mn(II) (phase I is of the polymanganite $\text{MnO}_n \cdot \text{MnO}_2 \cdot x\text{H}_2\text{O}$ type), Mn(III) (phase II is manganite MnOOH) and Mn(IV) (phase I and III – hydrated amorphous MnO_2). Air-drying at 100°C results in the dehydration of phase I with the formation of an amorphous product and decomposition of phase II to give Mn_2O_3 ($\gamma\text{-Mn}_2\text{O}_3$) and partial dehydration of III. Thus, the dried product is a mixture of amorphous polymanganite, $\gamma\text{-Mn}_2\text{O}_3$ and amorphous MnO_2 .

3. Heating in air, the following processes occur in the sample:

(i) 145 to 370°C – removal of fixed water

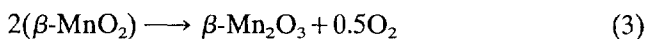


(ii) 395 to 470°C – oxidation of $\gamma\text{-Mn}_2\text{O}_3$

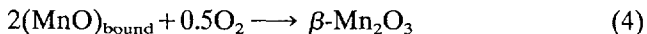


Within the same temperature range, crystallization of excessive MnO_2 into β -phase (pyrolusite) occurs:

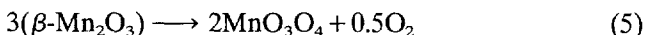
(iii) 559 to 595°C – decomposition of pyrolusite:



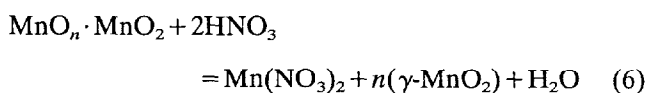
(iv) 695°C – oxidation of bound Mn(II):



(v) 960 to 990°C – decomposition of β -kurnakite:



4. The treatment with diluted nitric acid removes Mn(II) from the product:



5. Boiling the oxide with diluted nitric acid, a disproportionation of Mn(III) compounds takes place:



The final product – $\gamma\text{-MnO}_2$ – is practically identical to electrochemical manganese dioxide for its physicochemical properties. Fig. 3 shows discharge curves of the cathodic mass which consists of standard electrochemical $\gamma\text{-MnO}_2$ (EDM) and the oxide obtained by decomposition of nitrate solutions with subsequent treatment with HNO_3 in accordance with the above technique (CDM). Thus, the final product, $\gamma\text{-MnO}_2$, seems to be useful in cathodic masses of chemical power sources.

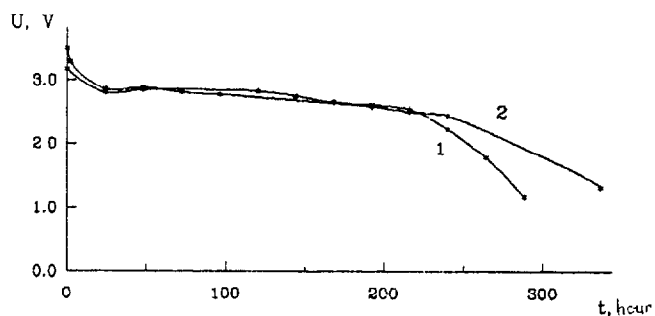


Fig. 3 Discharge curves of lithium cells with cathodes of (1) chemical manganese oxide CDM and (2) electrochemical manganese oxide EDM at $R=5.6 \text{ k}\Omega$

Acknowledgements

The authors acknowledge the help of A.N. Antishko, R.V. Tikhonova and K.I. Arsenin in carrying out the X-ray analysis, derivatography and IR spectroscopy.

References

- [1] Ye.Ya. Rode, *Oxygen-containing compounds of manganese Artificial compounds minerals and ores*, Izdatel'stvo Akademii Nauk SSSR, Moscow, 1952, p. 399.
- [2] H.K. Chakrabarti and T. Banerjee, *J. Sci. Ind. Res., Sect. B*, 12 (1953) 211–216.
- [3] K.J. Euler and R. Kurchhof, *Electrochim. Acta*, 26 (1981) 1383–1386.
- [4] L.I. Nyrkova, A.A. Andriiko and Ye.V. Kuz'minskii, *Ukr. Khim. Zh.*, 60 (1994) 312.
- [5] N.I. Sputnicov (ed.), *Complexometry Fundamentals and Applications*, Gos. Khim. Izdat., Moscow, 1958, p. 248.
- [6] A.K. Babko and I.V. Pyatnitskii, *Quantitative Analysis*, Gos. Khim. izdat., Moscow, 1956, p. 736.
- [7] M.M. Thackeray, M.H. Rossouw, A. de Kock, A.P. De la Harpe, R.J. Gummow, K. Heimberg and D.C. Lies, *6th Int. Meet. Lithium Batteries, Munster, Germany, 1992*, pp. 136–138.
- [8] T.E. Moorl, E. Marylenn and P.W. Selwood, *J. Am. Chem. Soc.*, 72 (1950) 856.
- [9] J.H. Bricker, *Am. Mineral.*, 50 (1965) 1296–1354.
- [10] W.K. Zwicker, W.O. Groeneveld-Meyer and H.W. Jaffe, *Am. Mineral.*, 47 (1962) 246.
- [11] G.A. Kolta, F.M. Abdel Kerim and A.A. Abdul Azim, *Z. Anorg. Allg. Chem.*, 384 (1971) 260–266.