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On the Crystal-Structure Change of Manganese Dioxide (CMD) during the Acid Digestion in $MnSO_4$–H_2SO_4 System

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Synopsis. The wet method to convert chemically prepared manganese dioxides (MnO_2s) into β-MnO_2 was reported. Chemically prepared MnO_2s, such as I. C. Sample Nos. 5, 8, 11, and 12, were converted into β-MnO_2 by using a proton-assisted rearrangement reaction in a boiling dil. H_2SO_4 solution containing Mn^{2+} ion at 100±10 °C.

In a previous paper,[1] the wet method to change crystal structures from several MnO_2s, such as δ-MnO_2, α-MnO_2, electrolytic MnO_2s (EMDs) and heat-treated EMDs to β-MnO_2 was reported and a complex situation in classifying artificial MnO_2s, especially prepared by wet methods, was discussed. In recent years, so-called chemically prepared MnO_2s (CMDs) in addition to EMDs became available for experimental use in batteries. In this paper, we report an extension of the method to some CMDs.

Experimental

CMDs, I. C. Sample Nos. 5, 8, 11, and 12, obtained from the International MnO_2 Sample Office (c/o Union Carbide Corp., Parma Technical Center, P. O. Box 6116, Cleveland, Ohio 44101, USA) were used as received. A reaction vessel was consisted of a 500 ml round-bottom flask joined to a condenser with the standard taper joint and a heating mantle at the bottom. A 250 ml of 0.5 mol dm^{-3} H_2SO_4 with 10 g of $MnSO_4$ (4—5)H_2O in a round-bottom flask was heated at 100±10 °C and then 10 g of MnO_2 sample was added into the flask. After the reaction period of a week, a reaction product was filtered and well-washed with cool distilled water. The washed reaction product was dried at about 60 °C in the air.

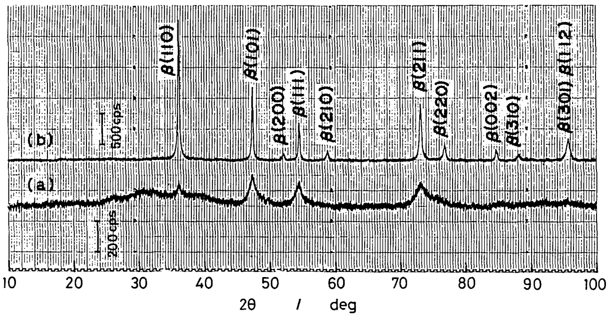

Fig. 1. X-Ray diffractional patterns of I.C. Sample No. 5 (a) and a reaction product (b) after the acid digestion of I.C. Sample No. 5 in 0.5 M H_2SO_4 (1 M= 1 mol dm^{-3}) with $MnSO_4$ at 100±10 °C for a week.

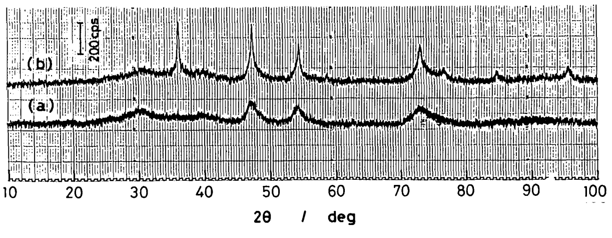

Fig. 2. X-Ray diffractional patterns of I.C. Sample No. 8 (a) and a reaction product (b) after the acid digestion of I.C. Sample No. 8 in 0.5 M H_2SO_4 with $MnSO_4$ at 100±10 °C for a week.

X-Ray data on starting materials and reaction products were obtained by using a Shimadzu XD-3A X-ray diffractometer with iron *K*α radiation (30 kV, 10 mA) filtered with manganese.

Results and Discussion

Since the location of line in terms of diffraction angle (2θ) and the shape of line were important in identifying the crystal structure of MnO_2, observed XRD patterns are shown in Figs. 1—4. The reaction product was identified as β-MnO_2 (pyrolusite) from both 2θ value (tetragonal system, a=4.39 Å and c=2.87 Å) and the intensities of lines ($P4_2/mnm\text{-}D_{4h}^{14}$ with the positional parameter of anion u=0.31), and the indices (h, k, l) are given in figures.

CMDs, such as I. C. Sample Nos. 5, 8, and 12, have almost the same XRD patterns, which may be

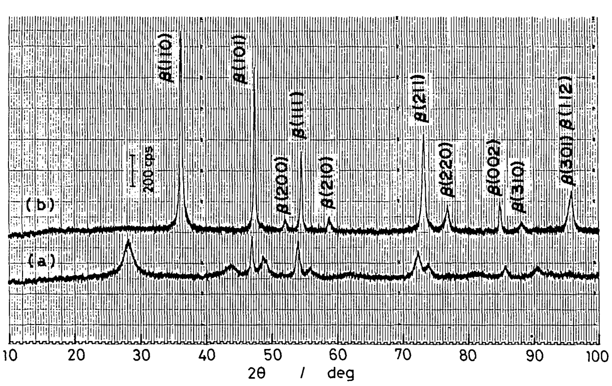

Fig. 3. X-Ray diffractional patterns of I.C. Sample No. 11 (a) and a reaction product (b) after the acid digestion of I.C. Sample No. 11 in 0.5 M H_2SO_4 with $MnSO_4$ at 100±10 °C for a week.

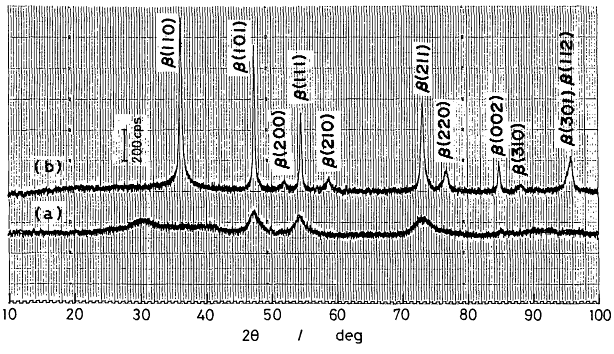

Fig. 4. X-Ray diffractional patterns of I.C. Sample No. 12 (a) and a reaction product (b) after the acid digestion of I.C. Sample No. 12 in 0.5 M H_2SO_4 with $MnSO_4$ at 100±10 °C for a week.

characterized by diffused lines at *ca.* 30 and 40° as shown in Figs. 1, 2, and 4. According to Gattow and Glemser,[2] they may be classified as γ-MnO_2.

The XRD pattern of I. C. Sample No. 11 has almost the identical 2θ values with those of ramsdellite[3] but the intensities are quite different, suggesting that the crystal structure is very close to ramsdellite but not exactly the same, which is probably due to the intergrowth of pyrolusite and ramsdellite domains[4] like nsutite.[5]

As can be seen in Figs. 1, 3, and 4, both types of CMDs, *i.e.*, I. C. Sample Nos. 5, 11, and 12, were converted into β-MnO_2. Although the XRD pattern of β-MnO_2 uncontaminated by the lines of starting material has not been obtained yet for some reasons, I. C. Sample No. 8 seems to be converted into β-MnO_2 after the acid digestion as is shown in Fig. 2. Without addition of $MnSO_4$ in a reaction mixture, none of the changes in XRD patterns was observed after the acid digestion.

Then, we conclude that CMDs available in the I. C. Sample Office can be converted into β-MnO_2 by using the proton-assisted rearrangement reaction in a boiling dil. H_2SO_4 solution containing Mn^{2+} ion at 100 ± 10 °C. The mechanism of the proton-assisted rearrangement reaction with Mn^{2+} ion is still under investigation by using spectro-electrochemical techniques combined with conventional analytical techniques.

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