Hydrothermal Soft Chemical Synthesis of Tunnel Manganese Oxides with Na^+ as Template

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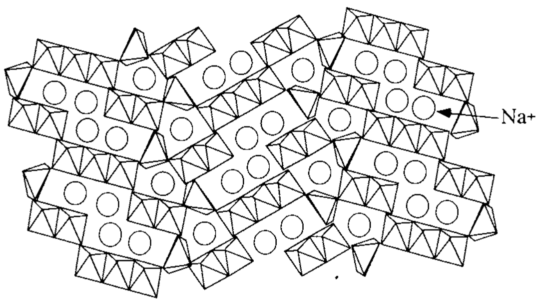
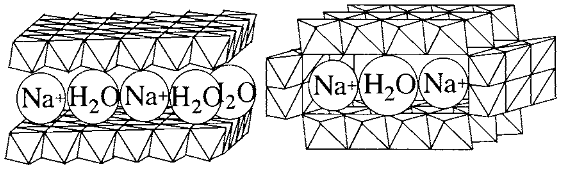
Na^+ was used as template in the synthesis of tunnel manganese oxides from a layered manganese oxide under hydrothermal conditions. Two types of tunnel manganese oxides were obtained by the hydrothermal reaction. The manganese oxide with a one-dimensional (2 × 4) tunnel structure formed under low temperature conditions, and $Na_{0.44}MnO_2$ with a one-dimension complex tunnel structure under high temperature conditions. The mechanism of the transformation reaction can be explained from the structures of the products and template size.

Manganese oxides with tunnel structures are interesting materials, due to their excellent ion-exchange, molecule adsorptive, and electrochemical properties. These manganese oxides can be used as ion-sieves,[1] molecule-sieves,[2] catalysts[3] and cathodic materials in lithium batteries.[4] Sodium manganese oxides with layered and tunnel structures, such as $NaMnO_2$ and $Na_{0.44}MnO_2$, have been used as the precursors for soft chemical synthesis of lithium manganese oxides with the similar layered and tunnel structures.[5,6] These lithium manganese oxides show good cycleabilities with high capacities as cathodic materials for rechargeable lithium batteries.[5,6] $Na_{0.44}MnO_2$ is a tunnel manganese oxide with a one-dimensional complex tunnel structure as shown in Figure 1(a).[7] This manganese oxide has been prepared by a solid state reaction[6,7] and a normal hydrothermal reaction.[8] In the hydrothermal synthesis, MnO_2 was hydrothermally treated in NaOH solution at high temperatures above 500 °C to obtained $Na_{0.44}MnO_2$.[8]



(a) $Na_{0.44}MnO_2$



(b) Na-Birnessite (c) (2×4) tunnel

Figure 1. Structures of manganese oxides with tunnel and layered structures.

Recently, we have proposed a hydrothermal soft chemical process for synthesis of tunnel and sandwich layered manganese oxides from a layer manganese oxide.[9-11] This process comprises two steps: the first step being preparation of a framework precursor with layered structure and insertion of template ions or molecules (structure-directing agents) into its interlayer space by a soft chemical reaction, and the second step transformation of the template-inserted precursor into a tunnel structure or a sandwich layered structure by hydrothermal treatment. Six kinds of tunnel manganese oxides have been obtained by using this method with Li^+, K^+, Mg^{2+}, and Ba^{2+} ions as the templates at low temperature hydrothermal conditions.[9,10] The dimension of the tunnel is dependent on the size of the used template. In the present study, we describe the synthesis of other tunnel manganese oxides with Na^+ as the template from a layered manganese oxide by using the hydrothermal soft chemical process.

An Na^+-form birnessite-type manganese oxide (NaBIR) was used as the precursor for the preparation of tunnel manganese oxides. NaBIR was obtained by pouring a mixed solution (100 mL) of 3% H_2O_2 and 0.6 M NaOH into a solution (50 mL) of 0.3 M $Mn(NO_3)_2$ with stirring, as described previously.[12] X-Ray diffraction analysis indicated that NaBIR has a layered structure with a basal spacing of 0.72 nm, which contains two-dimensional sheets of edge-shared MnO_6 octahedra with single crystal water sheets and Na^+ between the sheets of the MnO_6 octahedra (Figure 1(b)).[1,12]

NaBIR (0.5 g) and NaOH or NaCl solution (7 mL) were placed in a Hastelloy-C lined microautoclave (18 mL), and hydrothermally treated in a temperature range of 200 to 400 °C for one day under autogeneous pressure to transform the layered structure to tunnel structure. The X-ray diffraction studies indicated that the products of the hydrothermal reaction are dependent on the reaction solution and reaction temperature (Figure 2). In the 1 M NaCl solution, the layered structure of the birnessite retained below 300 °C, and transformed to Mn_2O_3 above 300 °C. In the NaOH solution, however, tow types of tunnel manganese oxides can be obtained. A manganese oxide with a one-dimensional (2 × 4) tunnel structure,[13] as shown in Figure 1(c), can be formed under the hydrothermal conditions of a temperature range from 200 to 300 °C and a concentration range of NaOH solution from 0.5 to 1.0 M. The (2 × 4) tunnel manganese oxide shows a low crystallinity, and only the main diffraction peaks can be confirmed on the X-ray diffraction pattern.

$Na_{0.44}MnO_2$ with the complex tunnel structure, as shown in Figure 1(a), can be obtained in NaOH solution above 250 °C by the hydrothermal reaction (Figure 2). In the higher concentration (4 M) of NaOH solution, $Na_{0.44}MnO_2$ can be formed at lower temperature (250 °C). Usually γ-Mn_2O_3 is also formed as an impurity under the high concentration conditions. $Na_{0.44}MnO_2$ of high purity can be obtained in the NaOH solu-

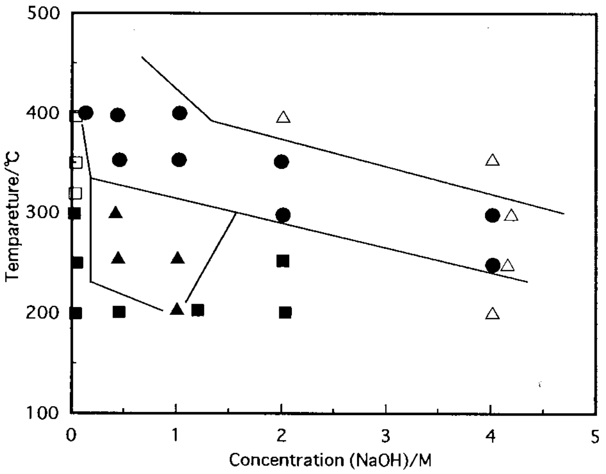


Figure 2. Dependence of the products on the reaction conditions. 0 M NaOH corresponds to 1 M NaCl. ■ : birnessite phase; ●: Na$_{0.44}$MnO$_2$ phase; ▲ : (2×4) tunnel phase; △ : γ-Mn$_2$O$_3$ phase; □ : Mn$_2$O$_3$ phase.

tions of lower concentration. The crystallinity of the tunnel manganese oxide increases with increasing reaction temperature. The X-ray diffraction pattern of the hydrothermal Na$_{0.44}$MnO$_2$ corresponds to that of the manganese oxide obtained by solid state reaction, except a diffraction peak with a d value of 0.6622 nm was observed in the hydrothermal manganese oxide.[7] This peak can be assigned to (040) diffraction. The crystal structure of the complex tunnel manganese oxide belongs to orthorhombic system (space group Pbm), and with lattice constants of **a** = 0.9086 nm, **b** = 2.641 nm, and **c** = 0.2827 nm.

The chemical compositional analysis on the manganese oxides indicated that the Na/Mn mole ratios are 0.31 for the birnessite, 0.36 for the (2 × 4) tunnel manganese oxide, and 0.45 for the Na$_{0.44}$MnO$_2$, which increase with increasing the reaction temperature. This result suggests that Na$^+$ can be inserted into the manganese oxides, accompanying reduction of tetravalent manganese to trivalent manganese during the hydrothermal reaction. Both of the tunnel manganese oxides have needle-like crystal morphology, and each needle axis of the crystal is along its axis of one-dimensional tunnel.

The above results reveal that the layered structure of the birnessite can be transformed to the (2 × 4) tunnel structure at lower temperature conditions than to the Na$_{0.44}$MnO$_2$ complex tunnel structure. This fact can be explained from the structures of the manganese oxides. The structural frameworks of the birnessite and the (2 × 4) tunnel manganese oxide consist of MnO$_6$ octahedral units. In the transformation reaction from the layered structure to the (2 × 4) tunnel structure, only a part of MnO$_6$ units change from edge-sharing position to the corner-sharing position, so that the reaction occurs easily even at low temperature. On the other hand, the transformation reaction from the layered structure to the Na$_{0.44}$MnO$_2$ tunnel structure causes not only change of a part of MnO$_6$ units from the edge-sharing position to corner-sharing position, but also change of a part of MnO$_6$ octahedra to MnO$_5$ square pyramids. The transformation reaction from MnO$_6$ octahedron to MnO$_5$ square pyramid would occur at higher temperature than the change of MnO$_6$ position.

The (2 × 4) tunnel manganese oxide of high crystallinity has been obtained by using Rb$^+$ as the template under the hydrothermal conditions.[13] Only the low crystalline (2 × 4) tunnel manganese oxide, however, was obtained by using Na$^+$ as template here. Na$^+$ is unsuitable as the template for the (2 × 4) tunnel structure, because the size of Na$^+$ is somewhat small for fitting the (2 × 4) tunnel size. The (2 × 4) tunnel structure with Na$^+$ as the template is unstable, and transforms to the Na$_{0.44}$MnO$_2$ tunnel structure under the high temperature conditions. On the other hand, in Na$_{0.44}$MnO$_2$ structure, the size of Na$^+$ just fits the tunnel size, so that the structure is stable at high temperature, and well crystalline Na$_{0.44}$MnO$_2$ can be obtained. The complex tunnel manganese oxide cannot been obtained by using Rb$^+$ as the template,[13] because the size of Rb$^+$ is too large for the complex tunnel.

By normal hydrothermal reaction with MnO$_2$ as starting material,[8] no (2 × 4) tunnel manganese oxide was formed and Na$_{0.44}$MnO$_2$ was obtained at higher temperature conditions than that with the layered manganese oxide as starting material. It can be concluded from these facts that the tunnel manganese oxides are formed easily from the layered manganese oxide, and the hydrothermal soft chemical process is a powerful method for the synthesis of the tunnel manganese oxides.

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