Transformation of manganese oxides from layered structures to tunnel structures

Qi Feng,* Kazumichi Yanagisawa and Nakamichi Yamasaki

Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, 2-5-1 Akebono-cho, Kochi-shi 780, Japan

Birnessite-type manganese oxide can be transformed to tunnel structures by hydrothermal treatment.

There are many types of manganese oxides with tunnel and layered structures,[1] since manganese oxides have the characteristics of both ready conversion between Mn^{IV} and Mn^{III} and formation of defects in the crystals. Since metal ions and organic molecules can be topotactically inserted and extracted into and from the tunnel and the interlayer space of manganese oxides, these oxides can be used as ion sieves,[2–11] molecule sieves,[12,13] catalysts,[14,15] and cathodic materials in lithium batteries.[16–18] Manganese oxides can be prepared by solid-state,[2–7] solution phase,[8,9,17,18] or hydrothermal reaction.[10,19] Recently, it has been reported that a Mg^{2+}-exchanged birnessite-type manganese oxide with a layered structure can be transformed to todorokite-type magnesium manganese oxide which has a one-dimensional (3 × 3) tunnel structure by hydrothermal treatment.[11–13,20] The hydrated Mg^{2+} in the interlayer space of the birnessite structure serves as a template for the (3 × 3) tunnel structure. This fact suggests that it may be possible to obtain manganese oxides with different tunnel sizes by hydrothermally treating a layered manganese oxide subsequent to insertion of cations of different sizes, acting as a template, into the interlayer space. Here, we describe transformation reactions from Li^+-, K^+- and Mg^{2+}-exchanged birnessite-type manganese oxides into manganese oxides with tunnel structures under hydrothermal conditions.

A Na^+-form birnessite (BirMO–Na) was prepared by mixing a solution (100 ml) of 3% H_2O_2 and 0.6 mol dm^{-3} NaOH with a solution (50 ml) of 0.3 mol dm^{-3} $Mn(NO_3)_2$ under stirring. X-Ray diffraction analysis (Fig. 1) indicated that BirMO–Na has a layered structure with a basal spacing of 7.2 Å, containing two-dimensional sheets of edge-shared MnO_6 octahedra, with single-crystal water sheets and Na^+ between the sheets of the MnO_6 octahedra [Fig. 2(*a*)].[10,11,19] After treating BirMO–Na (5 g) with 1 mol dm^{-3} LiCl, KCl and $MgCl_2$ solutions (1 l) for 1 day, Li^+-, K^+- and Mg^{2+}-exchanged birnessites BirMO–Li, BirMO–K and BirMO–Mg were obtained, respectively (Table 1). Ion-exchange treatment was repeated three times to ensure complete exchange of all Na^+ in BirMO–Na. The layered structure remained after Li^+, K^+ and Mg^{2+} exchange, but the basal spacings changed to 7.1, 7.2 and 9.7 Å, respectively. BirMO–Mg contains double-crystal water sheets between the

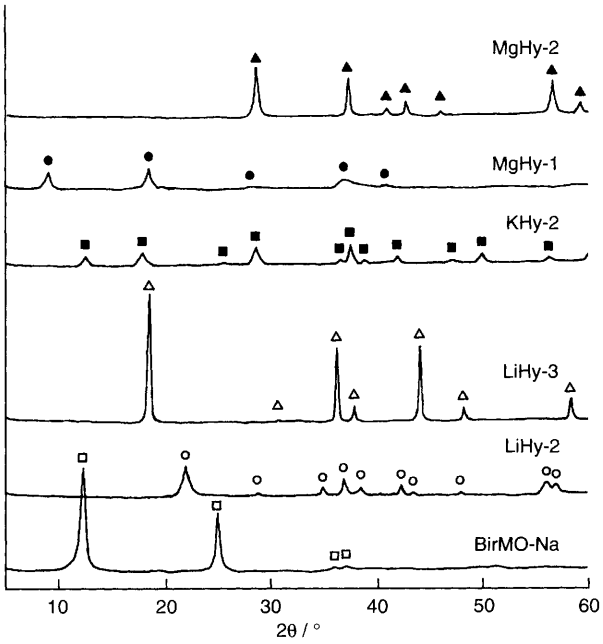


Fig. 1 X-Ray diffraction patterns of the starting material BirMo–Na and the hydrothermally treated samples with tunnel structures (LiHy-2, LiHy-3, KHy-2, MgHy-1 and MgHy-1). (□) Birnessite phase,[9,18] (○) ramsdellite phase (ASTM 39-375), (△) spinel phase,[6] (■) hollandite phase,[8,9] (●) todorokite phase,[11,21] (▲) pyrolusite phase (ASTM 24-735).

Table 1 Reaction conditions, compositions, and crystal structures of manganese oxides

Sample	Reaction solution	M : Mn molar ratio[a]	Crystal structure
Starting material			
BirMO–Na	—	0.272	Birnessite
Ion-exchanged sample			
BirMO–Li	—	0.223	Birnessite
BirMO–K	—	0.297	Birnessite
BirMO–Mg	—	0.156	Birnessite
Hydrothermally treated sample			
LiHy-1	1 mol dm^{-3} LiCl	0.236	Birnessite
LiHy-2	0.5 mol dm^{-3} H_2SO_4–1 mol dm^{-3} LiCl	0.003	Ramsdellite
LiHy-3	0.1 mol dm^{-3} LiOH	0.470	Spinel
KHy-1	1 mol dm^{-3} KCl	0.305	Birnessite
KHy-2	0.5 mol dm^{-3} H_2SO_4–1 mol dm^{-3} KCl	0.161	Hollandite
KHy-3	0.1 mol dm^{-3} KOH	0.312	Birnessite
MgHy-1	1 mol dm^{-3} $MgCl_2$	0.176	Todorokite
MgHy-2	0.5 mol dm^{-3} H_2SO_4–1 mol dm^{-3} $MgCl_2$	0.000	Pyrolusite

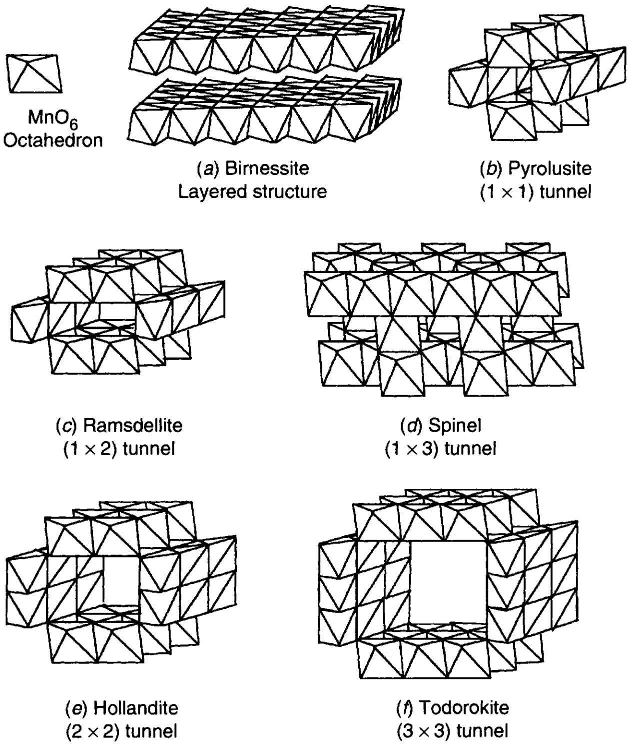
[a] M = Na, Li, K or Mg

sheets of the MnO_6 octahedra due to the strong hydration effect of Mg^{2+}.[11,20]

BirMO–Li, BirMO–K and BirMO–Mg were autoclaved with the solutions shown in Table 1 at 150 °C for 2 days under autogenous pressure. The hydrothermally treated samples (LiHy-1, LiHy-2, LiHy-3, KHy-1, KHy-2, KHy-3, MgHy-1 and MgHy-2) were investigated by X-ray diffraction, FTIR, and chemical analyses. The compositions and structures of the hydrothermally treated samples are summarized in Table 1, and the X-ray diffraction patterns of the tunnel-structure samples are shown in Fig. 1.

The birnessite structure of BirMO–Li was transformed to ramsdellite and spinel structures (LiHy-2 and LiHy-3) after hydrothermal treatment in a mixed solution of 0.5 mol dm^{-3} H_2SO_4–1 mol dm^{-3} LiCl–0.1 mol dm^{-3} LiOH solution, respectively, while BirMO–Li retained the birnessite structure (LiHy-1) after hydrothermal treatment in LiCl solution. BirMO–K was transformed to a hollandite structure (KHy-2) after hydrothermal treatment in 0.5 mol dm^{-3} H_2SO_4–1 mol dm^{-3} KCl, and the birnessite structure was retained after hydrothermal treatment in 1 mol dm^{-3} KCl–0.1 mol dm^{-3} KOH solution. A todorokite- (MgHy-1) and a pyrolusite-type manganese oxide (MgHy-2) were obtained by hydrothermally treating BirMO–Mg in 1 mol dm^{-3} $MgCl_2$ solution and in a mixed solution of 0.5 mol dm^{-3} H_2SO_4–1 mol dm^{-3} $MgCl_2$, respectively.

The pyrolusite, ramsdellite, spinel, hollandite and todorokite-type manganese oxides have one-dimensional (1 × 1), one-dimensional (1 × 2), three-dimensional (1 × 3), one-dimensional (2 × 2) and one-dimensional (3 × 3) tunnel structures, respectively, as shown in Fig. 2.[1,6] The transformations from the birnessite structure to the spinel, hollandite and todorokite structures are due to the fact that Li^+, K^+, and hydrated Mg^{2+} act as templates to direct the structures. Our previous studies have indicated that the sizes of Li^+, K^+ and hydrated Mg^{2+} ideally fit the three-dimensional (1 × 3) tunnel of spinel, one-dimensional (2 × 2) tunnel of hollandite and one-dimensional (3 × 3) tunnel, respectively.[6,7,9–11] LiHy-2 and MgHy-2 have ramsdellite and pyrolusite structures with smaller tunnel sizes than the spinel in which the metal ions do not act as templates in the transformation reactions with Li^+ and Mg^{2+} dissolving from the solid phase into the acidic solution (Table 1).



(*a*) Birnessite
Layered structure

(*b*) Pyrolusite
(1 × 1) tunnel

(*c*) Ramsdellite
(1 × 2) tunnel

(*d*) Spinel
(1 × 3) tunnel

(*e*) Hollandite
(2 × 2) tunnel

(*f*) Todorokite
(3 × 3) tunnel

Fig. 2 Structures of manganese oxides with layered and tunnel structures

The above facts suggest that manganese oxides with different tunnel sizes can be obtained by hydrothermally treating a manganese oxide of layered structure after insertion of cations with different sizes into the interlayer spaces. Since this process comprises two steps: the first step being a soft chemical reaction (insertion of template ions into the interlayer space), and the second step a hydrothermal reaction (transformation of the layered structure into a tunnel structure), we designate this process as a 'hydrothermal–soft chemical reaction'. Synthetic studies on other manganese oxides with tunnel structures obtained by this process are currently being undertaken.

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