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# Preparation of todorokite-type manganese-based oxide and its application as lithium and magnesium rechargeable battery cathode

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## Abstract

Todorokite type  $Mg_xMnO_2 \cdot yH_2O$  which possesses  $3 \times 3$  large tunnel structure was prepared through hydrothermal treatment of layer manganese dioxide, buserite, at  $120\text{--}200^\circ\text{C}$ . In non-aqueous Li and Mg cells, electrochemical insertion of  $Li^+$  and  $Mg^{2+}$  into the todorokite products occurred utilizing the preferable large tunnel for their diffusion. By heat-treatment up to  $300^\circ\text{C}$ , cycle performances in Li cell were improved by removing water molecules from the todorokite tunnel. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Manganese oxide; Todorokite; Intercalation; Lithium battery; Magnesium

## 1. Introduction

Manganese oxides have long been studied for their use as catalytic materials and in battery applications. There are various manganese-based oxide frameworks which are roughly classified into tunnel structures (1D), layer phases (2D), and spinels (3D) [1].

Fig. 1a shows three types of square-tunnel structures based on manganese dioxide called as pyrolusite ( $1 \times 1$ ), hollandite ( $2 \times 2$ ) and todorokite ( $3 \times 3$ ). Among them, “todorokite” has largest tunnel structure, which consists of triple chains of edge-sharing  $MnO_6$  octahedra that form  $3 \times 3$  channels [2]. Recently, the synthesis of a thermally stable todorokite by means of combination of aqueous solution and hydrothermal techniques was developed by Suib and coworkers [3–5], and first row transition metals ( $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Mg^{2+}$ ) were doped into the framework [6]. Further, a few reports appeared in a viewpoint of the lithium battery application of the synthetic todorokite [7–9]. For the application as a host for electrochemically reversible intercalation of lithium, vacant spacing in the host plays an important role to improve the intercalation dynamics. In this paper, we report the fundamental properties and relationship between the synthetic condition and cathode performance of the todorokite in Li and Mg cells.

## 2. Experimental

The todorokite manganese oxide were prepared according to the previous literature [3] as follows: at first, to synthesize layered birnessite  $Na_xMnO_2$ ,  $Mn(OH)_2$  was precipitated by addition of 50 ml of  $5.0 \text{ mol dm}^{-3}$  NaOH solution into 40 ml of  $0.50 \text{ mol dm}^{-3}$   $MnCl_2$  solution under vigorous stirring. This  $Mn(OH)_2$  was oxidized by adding  $0.10 \text{ mol dm}^{-3}$   $NaMnO_4$  at a molar ratio of  $Mn(OH)_2/NaMnO_4 = 0.4$  at room temperature to obtain layered birnessite  $Na_xMnO_2$  powder. It was aged for 1 week and then filtered and washed. Ion-exchange of the  $Na^+$  for  $Mg^{2+}$  was achieved by dispersing the birnessite in  $1.0 \text{ mol dm}^{-3}$   $MgCl_2$  solution for 1 day to obtain buserite  $Mg_xMnO_2$ . Todorokite manganese oxide was prepared by hydrothermal treatment ( $120\text{--}200^\circ\text{C}$ ) of the Mg–buserite for 4 days in pure water. Finally, products was vacuum dried at room temperature.

The obtained samples were identified by powder X-ray diffraction (XRD) using Cu  $K\alpha$  radiation. The elemental analyses of obtained samples were performed by atomic absorption spectrometry (for Na and Mn determination) and chelatometric titration (for Mg determination). Water content was measured from weight loss by heating at  $300^\circ\text{C}$  for 3 h.

Electrochemical lithium de/insertion was investigated using beaker-type cell at  $25 \pm 2^\circ\text{C}$ . As working electrodes, the mixtures of the sample and graphite (in a weight ratio 1:1) were compression molded on an Ni net. Lithium was used as the reference and counter electrodes. The electrolyte used was  $1 \text{ mol dm}^{-3}$   $LiClO_4$ –propylene carbonate (PC).

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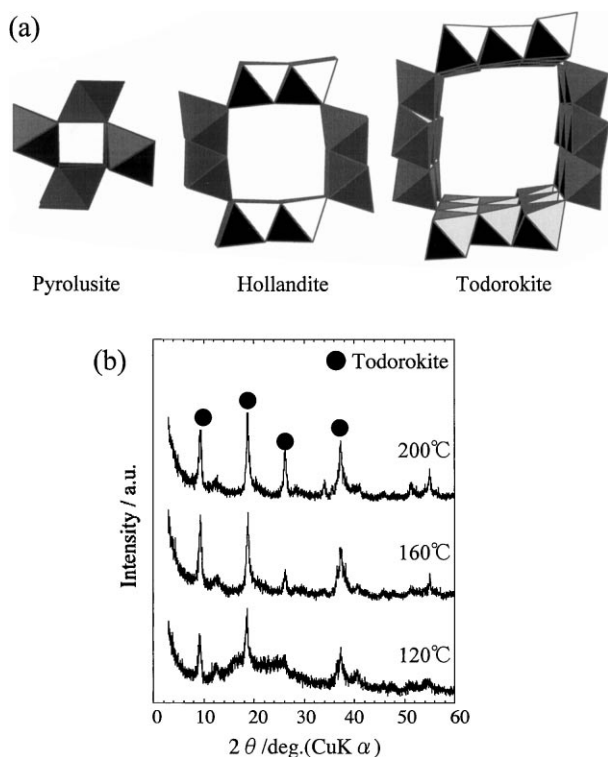


Fig. 1. (a) Crystal structure models of three manganese oxides with a tunnel structure (pyrolusite, hollandite and todorokite) and (b) X-ray diffraction patterns of synthesized manganese oxide samples.

These tests were carried out between 2.0 and 4.2 V versus Li/Li<sup>+</sup> at 0.1 mA cm<sup>-2</sup>.

Electrochemical magnesium de/insertion were also investigated similarly. Todorokite and hollandite were used as active materials. Hollandite was synthesized by addition of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> into boiling 1 mol dm<sup>-3</sup> MnSO<sub>4</sub> aqueous solution [10]. Magnesium metal was used as the reference and counter electrodes. The electrolyte used was 1 mol dm<sup>-3</sup> Mg(ClO<sub>4</sub>)<sub>2</sub>-PC. These tests were carried out between 1.32 and 3.32 V versus Mg/Mg<sup>2+</sup> (corresponding to 2.00 and 4.00 V versus Li/Li<sup>+</sup>).

### 3. Results and discussion

Fig. 1b shows powder XRD patterns of products obtained by the hydrothermal treatment of buserite at 120, 160, and 200°C. It is clear that the peaks corresponding to todorokite phase appear at 2θ = 9.36, 18.7, 26.2 and 37.3° in the XRD pattern. With rising the hydrothermal temperature, the peaks are becoming higher and sharper. Their crystallinity, hence was gradually improved by increasing of the hydrothermal treatment.

Table 1 shows the chemical compositions and oxidation state of Mn of samples synthesized in this work. As mentioned above, birnessite and buserite were used as the precursor for the synthetic todorokite. The values of *x* in Mn<sup>x+</sup> of all samples were approximate 3.65. A quantity of

Table 1

Chemical composition and mean oxidation state of Mn in synthesized samples

Sample	Composition	<i>x</i> in Mn <sup>x+</sup>
Na–birnessite	Na <sub>0.32</sub> MnO <sub>1.99</sub> ·0.30H <sub>2</sub> O	3.66
Mg–buserite	Mg <sub>0.13</sub> MnO <sub>1.96</sub> ·0.73H <sub>2</sub> O	3.66
Todorokite: 200°C	Mg <sub>0.14</sub> MnO <sub>1.96</sub> ·0.32H <sub>2</sub> O	3.64
Todorokite: 160°C	Mg <sub>0.21</sub> MnO <sub>2.03</sub> ·0.24H <sub>2</sub> O	3.63
Todorokite: 120°C	Mg <sub>0.26</sub> MnO <sub>2.09</sub> ·0.55H <sub>2</sub> O	3.65

water molecule in Mg–buserite is twice as much as that in birnessite, since one layer of water molecules should be existing between the MnO<sub>2</sub> layers in Na–birnessite, and two layers of water molecules are existing between the MnO<sub>2</sub> layers in buserite [1]. During hydrothermal treatment of buserite, todorokite structure was formed through rearrangement of MnO<sub>6</sub> octahedra. Simultaneously, the water content was decreased, and the Mg/Mn ratio was increased by the hydrothermal rearrangement. In the three todorokites, the Mg contents decreased from 0.26 to 0.14 with increasing the hydrothermal temperature from 120 to 200°C, maintaining the mean oxidation of manganese.

These todorokites were examined as an electrochemical insertion host for battery cathode materials. Fig. 2 shows discharge/recharge curves of the todorokite electrodes in Li cells, which contained some magnesium ions and waters in the structure. The electrodes exhibited high electoractivity in Li cell due to lithium de/insertion. From the curves, all samples show potential plateau in the region around 3 V. These shapes of curve are similar to other typical MnO<sub>2</sub> materials. The todorokite obtained at 200°C performed the

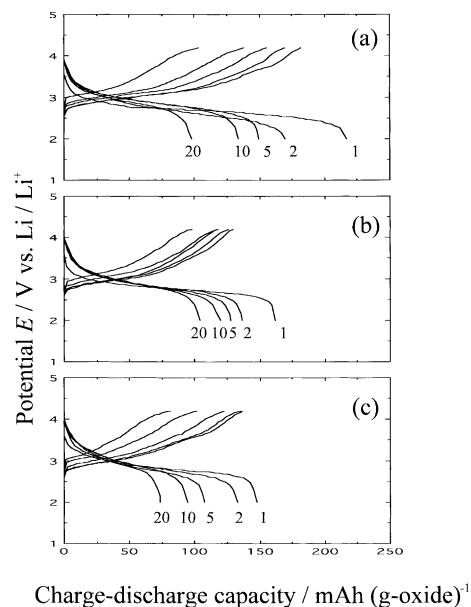


Fig. 2. Discharge/recharge curves of synthesized todorokite manganese oxides in Li cell which were synthesized at hydrothermal temperature of (a) 200; (b) 160, and (c) 120°C.

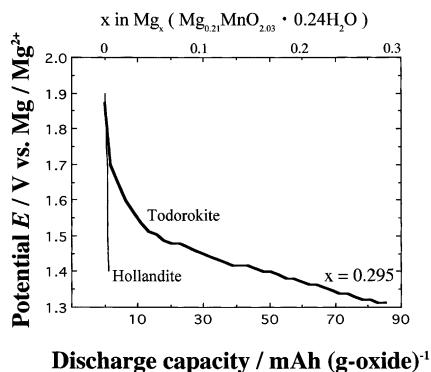


Fig. 3. Initial discharge curves of hollandite and todorokite obtained at hydrothermal temperature of 160°C in Mg cell.

highest capacity of ca. 220 mAh (g-oxide)<sup>-1</sup> at the initial, corresponding to amount of inserted lithium, 0.74, and the capacity of greater than 100 mAh g<sup>-1</sup> was maintained during the initial 20 cycles.

According to [3,8], the water molecules existing in large tunnel were hydrated waters of Mg<sup>2+</sup> ion. It is expected that lithium insertion would be improved by removing the water because of the formation of the larger vacant tunnel. Hence, the todorokite was heat treated at 200, 300 and 400°C. As a result, although the todorokite was transferred to Mn<sub>2</sub>O<sub>3</sub> by heat treatment at 400°C, there was almost no change in XRD pattern up to 300°C. From thermogravimetry (10°C min<sup>-1</sup>) for the todorokite obtained hydrothermally at 160°C, the weight loss gradually occurred from room temperature to 400°C.

When discharge/recharge examination was carried out for the three todorokite samples (Table 1) which were heat treated at 200°C in air for 1 h, the initial discharge capacity was increased for all sample. Especially, the initial discharge capacity of sample synthesized at 120°C increased to 204 mAh g<sup>-1</sup>, and then it exhibited of the discharge capacity 150 mAh g<sup>-1</sup> even after the initial 10 cycles. Thus, it was found that remove of water molecules leads to increasing discharge capacity. It would be due to the enhancement of lithium diffusion of dynamics in the tunnel.

It is generally known that Mg insertion into oxide materials is difficult and hardly reversible [11], because of highly charging of Mg<sup>2+</sup> ion compared with that of Li<sup>+</sup> ion. We

expected that todorokite could show higher electroactivity of Mg<sup>2+</sup> insertion on account of the fact that the todorokite structure is stabilized by Mg<sup>2+</sup> ion in the tunnel. As shown in Fig. 3, todorokite exhibited higher capacity compared to hollandite which has a 2 × 2 smaller tunnel. Fig. 3 shows the initial discharge (electrochemical reduction) curves of todorokite and hollandite electrodes. Discharge capacity by Mg insertion into todorokite is 85 mAh g<sup>-1</sup>, corresponding to the amount of inserted Mg, ca. 0.3. On the other hand, Mg insertion hardly happened into hollandite. It is known that Mg<sup>2+</sup> ion has a large solvation energy, so that it is considered that the insertion becomes possible in bigger tunnel size of 3 × 3.

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