Synthesis of Hollandite-Type Manganese Dioxide with H⁺ Form for Lithium Rechargeable Battery

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ABSTRACT

A hollandite-type manganese dioxide (HoIMO), without foreign metal cations (K⁺, NH₄⁺, Na⁺) in the (2 × 2) tunnel, was prepared directly by reacting LiMnO₄ with Mn(NO₃)₂ in an H₂SO₄ acidic solution. The HoIMO belonged to a body-centered tetragonal system (space group I4/m) and could be expressed by the formula H_{4x}Mn_{8-x}O₁₆ · yH₂O. A preliminary electrochemical study suggested that the HoIMO is promising as the cathode for a lithium rechargeable battery.

In recent years, much interest has centered upon the development of lithium rechargeable batteries with high energy densities. A large number of studies have been reported on the charge-discharge characteristics of batteries with the cathodes of spinel-type manganese oxides which have a three-dimensional (1 × 3) tunnel for lithium-ion transport.¹⁻⁵ However, there has been very little attention given to hollandite- or cryptomelane-type manganese oxides⁶ which have a one-dimensional (2 × 2) tunnel structure, as is shown in Fig. 1. It is expected that the lithium-ion transport will be easier in the (2 × 2) tunnel than in the (1 × 3) tunnel.

The hollandite-type manganese oxides are synthesized conventionally by precipitation from an Mn(II) solution with an oxidizing agent such as KMnO₄, K₂S₂O₈, or their ammonium or sodium salts. The manganese oxides prepared by this method contain K⁺, NH₄⁺, or Na⁺ ions in the (2 × 2) tunnel. These metal ions will block the lithium-ion transport through the (2 × 2) tunnel. They can be extracted from the tunnel by treating with concentrated HNO₃ (13*M*),⁷ but complete extraction is very difficult, since K⁺ or NH₄⁺ ions are tightly fixed on the (2 × 2) tunnel. A recent report has shown that H⁺ form hollandite-type (or alpha) manganese dioxide can be obtained by H₂SO₄ treatment of Li₂MnO₃ at 90°C, and the manganese dioxide shows a good rechargeable property.⁸

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Fig. 1. Structure of hollandite-type manganese oxide. The MnO_6 -octahedra link together, sharing edges to form the (2 × 2) tunnel structure.

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Fig. 2. X-ray diffraction patterns of manganese oxides prepared at different H_2SO_4 concentrations. O: hollandite phase; Δ : γ -MnO₂.

The present paper describes a new method of obtaining hollandite-type manganese dioxide directly by reacting LiMnO₄ with $Mn(NO_3)_2$ solution. Since the HolMO contains only a very small

Table I. Compositional and structural parameters of the hollandite-type manganese dioxide.

Sample	Z_{Mn}	Li/Mn	K/Mn	H₂O/Mn	Lattice constant (A)		
					а	С	a/c
HolMO ^a	4.01	0.001	_	0.31	9.80	2.86	3.43
α -MnO ₂ ^b	4	0.004		0.3	9.78	2.85	3.43
CryMO ^{c̄}	—	—	0.006	0.28	9.77	2.85	3.43

^a Sample prepared here.

^b Ref. 8.



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Fig. 3. First discharge-charge curves of Li/HoIMO cell with a current rate of 0.25 mA/cm² at 25°C.

amount of foreign metal ions (Li^+), it has promise as a cathode for a lithium secondary battery.

Experimental

Manganese oxides were prepared by slowly adding a 0.1M LiMnO₄, solution to a 0.1M Mn(NO₃)₂ solution containing H₂SO₄ of varied concentrations while stirring at 100°C. The mixed solution was kept at 100°C for 2 h, and then at 50°C for 1 day. The product was filtered, washed with water, and air-dired. Chemical, x-ray, and DTA-TG analysis and a pH titration study were carried out by the method described in a previous paper.⁹

The electrochemical cell used was LiLiClO₄ in DME, PCHoIMO. A mixture of HoIMO (70 wt% after drying at 300°C), acetylene black (25 wt%), and Teflon binder (5 wt%) was used as a cathode, a polypropylene nonwoven cloth as a separator, an LiClO₄ (10 wt%) propylene carbonate (PC)/dimethoxyethane (DME) (1:1 by weight) solution as electrolyte, and a lithium-aluminum alloy sheet as an anode.

Results and Discussion

The formation of the hollandite phase is greatly dependent on the acidity of the reacting solution, as is shown in Fig. 2. The γ -MnO₂ phase is formed when the H₂SO₄ concentration is below 1*M*. The proportion of the hollandite phase increases with the increase of H₂SO₄ concentration in the region above 1*M*. Pure hollandite phase is observed when the H₂SO₄ concentration is higher than 8*M*. The



Fig. 4. Plot of discharge (\Box) and charge (+) capacities *vs.* cycle number for Li/HoIMO cell.

formation of the hollandite phase was also dependent on the mole ratio of LiMnO₄ to Mn(NO₃)₂; the best mole ratio was 1:1. The yield of the HolMO was higher than 90% when it was prepared in the conditions LiMnO₄:Mn(NO₃)₂ = 1:1 and 8*M* H₂SO₄. The x-ray diffraction data indicate that the crystal has a (2 × 2) tunnel structure which belongs to a body-centered tetragonal system (space group I4/m) (Fig. 1). The lattice parameters are in good agreement with those reported on H⁺ form α -MnO₂⁺⁸ and K⁺-extracted cryptomelane⁷ (Table I). The DTA-TG analysis shows that the hollandite structure is stable enough up to 400°C.

Chemical analysis revealed that the HolMO contains only a small amount of Li⁺, and has the mean oxidation number of manganese (Z_{Mn}) of 4.01 (Table I). This indicates that the sample has a composition corresponding to manganese dioxide. The stoichiometry of the HolMO can be written as $MnO_2 \cdot 0.31H_2O$ from the analytical results. A pH titration study showed that the HolMO has lattice protons which can exchange with lithium ions in LiOH solution. Therefore, the HolMO can be expressed by the formula $H_{4x}Mn_{8-x}O_{16} \cdot yH_2O$, where *x* is the number of defects at the manganese site and *y* the number of crystal water which may occupy the (2 × 2) tunnel site. The number of lattice protons (4*x*) is four times that of the manganese defect.

A preliminary electrochemical study was carried out on the Li/ HolMO cell. First discharge-charge curves of the cell with a current rate of 0.25 mA/cm² at 25°C are given in Fig. 3. The dischargecharge curves indicate that the lithium insertion and extraction with HolMO are nearly reversible electrochemical processes. The first discharge gives a capacity of 230 mAh/g from 3.8 to 2.0 V which is about 10% higher than those on hollandite-type manganese oxides in the literature.^{6,8} The discharge capacity suggests that about six lithium ions can be inserted into one unit cell of the hollandite structure. The inserted lithium ions may occupy the (2×2) tunnel sites. Ohzuku et al. have proposed that the lithium ions may also occupy the (1×1) tunnel sites of the hollandite structure.⁶ A discharge-charge cycling test was carried out between 4.0 and 2.0 V. The cell capacity drops slightly to about 170 mAh/g after 3 cycles and then remains almost constant until 10 cycles (Fig. 4). The Li/HolMO cell in the present study shows much higher cycling stability than that in the literature.⁸ X-ray diffraction study indicated that there is no damage on the hollandite structure after the dischargecharge cycling test.

A HolMO sample treated with LiOH solution also showed a good discharge-charge property as the cathode. A more detailed electrochemical study is currently being carried out.

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