

## 論文の内容の要旨

論文題目     Electrode Properties of Tunnel-Structured  
MnO<sub>2</sub> for Mg-ion Secondary Batteries  
(トンネル構造マンガン酸化物のマグネシウムイオン電池電極特性)

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Magnesium ion batteries present an alternative to lithium ion batteries due to their high energy density, safe operation and low cost, especially in context of large-scale applications like electric vehicles and electrical energy storage systems (EES) connected to smart grid. MnO<sub>2</sub> is very exciting electrode material that has been utilized as an insertion electrode for lithium ion secondary batteries and electrochemical capacitors due to its unique crystal structure, environmental friendly behavior, and easy availability at low cost. However, MnO<sub>2</sub> has not been widely researched as an electrode material for magnesium ion rechargeable batteries.

The unique tunnel structures and very exciting electrochemical properties of MnO<sub>2</sub> can offer great advantages for migration of divalent Mg<sup>2+</sup> ions. In this study, in order to elucidate the possible employment of tunnel-structured MnO<sub>2</sub> as the cathode materials for Mg-ion secondary batteries, their electrochemical properties are investigated. As the electrode MnO<sub>2</sub> materials, layer-structured Birnessite-MnO<sub>2</sub> (Bir), tunnel-structured OMS-5-MnO<sub>2</sub> (OMS-5) and tunnel-structured Hol-MnO<sub>2</sub> (Hol) are used. In addition, microstructure of the electrode materials is designed during pre-synthesis or post-synthesis, to accomplish optimum Mg-ion reversible insertion/extraction properties.

Chapter 1 discusses the background of this study, which comprises of introduction to rechargeable lithium ion batteries (LIB), magnesium ion batteries (MIB), the cathode materials and the objectives of this study.

In chapter 2, synthesis procedures of pure  $\text{MnO}_2$  and composite  $\text{MnO}_2$ /acetylene black (AB) are described, and chapter 3 explains the electrochemical characterization methods. The active materials based on various polymorphs of  $\text{MnO}_2$ , are synthesized successfully as pure  $\text{MnO}_2$  and  $\text{MnO}_2$ /acetylene black (AB) composite materials through sol-gel and hydrothermal synthesis methods. The purpose of fabricating the  $\text{MnO}_2$ /AB composites is to improve the low intrinsic electronic conductivity of hydrous  $\text{MnO}_2$  polymorphs. X-ray diffraction (XRD) analysis confirms the single-phase materials irrespective of the synthesis method used. Scanning electron microscopy (SEM) shows flake like morphology of layer-structured Birnessite- $\text{MnO}_2$ , while fiber like morphology is observed for tunnel structured materials.  $\text{MnO}_2$  active materials are characterized under galvanostatic and potentiostatic conditions using Mg as counter electrode and titanium (Ti) as current collectors.  $\text{Ag}/\text{Ag}^+$  is used as reference electrode and 1M  $\text{Mg}(\text{ClO}_4)_2/\text{AN}$  is used as electrolyte. All of the electrode assembly is carried out in a glove box.

In chapter 4, electrochemical properties of pure  $\text{MnO}_2$  as Mg-ion insertion/extraction electrodes are described. From the charge/discharge profiles, the specific capacities calculated for various  $\text{MnO}_2$  samples are found to increase in the following order; Birnessite < OMS-5 < Hollandite. Furthermore, there is very large difference between charge-discharge potentials, observed during electrochemical process, which results from slow kinetics of Mg-ion migration. Electrochemical results demonstrate the sufficient charge-discharge cyclic performance.

In chapter 5, electrochemical performance of  $\text{MnO}_2$ /AB composite as Mg-ion insertion/extraction electrodes is explained. The low electronic conductivity of hydrous  $\text{MnO}_2$

structures is improved by the addition of AB and the specific capacity of each composite material is improved to a great extent, when compared to pure MnO<sub>2</sub> materials. Hol/AB exhibited the largest initial discharge capacity, which increases in the following order; Mg-Bir/AB (109 mAh/g) <OMS-5/AB (141 mAh/g) <Hol (209 mAh/g). Electrochemical measurements results suggest that, although addition of AB improved the capacity of composite powders, low intrinsic electronic and low ionic conductivity of Bir/AB and OMS-5/AB, might be responsible for limited Mg-ion insertion in these structures. Moreover, the results demonstrate that there is no direct relationship between tunnel sizes of the host lattice with the Mg-ion insertion, but several other factors, such as BET surface area and amount of crystalline water present in the tunnels/layers, are important as well and govern the ionic movement within the structure.

Due to better Mg ion insertion properties of Hol when compared to other polymorphs of MnO<sub>2</sub>, Hol/AB is selected for further studies and amount of the AB in the Hol/AB composite is reduced. The composite comprising of 65 wt% Hol and 35 wt% AB (65/35) shows the highest discharge capacity of 310 mAh/g in comparison to Hol/AB (75/25) and Hol/AB (85/15). Simultaneous effect of the optimum pore size of the composite and complete distribution of AB along the Hol particles is considered to be the source for such a large capacity of Hol/AB (65/35). Besides the substantial Mg-ion insertion/extraction, the tunnel framework of the Hol/AB is retained with minor structural adjustments, but large capacity loss is observed after several cycles.

In chapter 6, factors influencing the Mg ion insertion/extraction kinetics have been examined. Results demonstrate that Mg ion insertion/extraction properties are enormously improved and a large capacity (475 mAh/g) is attained at a higher temperature of 60°C. The adverse effect of stabilizing K<sup>+</sup> ion residing in the tunnel against Mg-ion movement is reduced

by removing  $K^+$  ion from the tunnel and results indicate better discharge capacity ( $372 \text{ mAhg}^{-1}$ ) suggesting that defect free tunnel improves the Mg-ion migration. Moreover, the maximum discharge capacity of  $532 \text{ mA/g}$  is achieved by decreasing the diffusion length of particles through ball milling. This is the largest capacity of any  $\text{MnO}_2$  host according to best of our knowledge to the date.

Chapter 7 describes the study to seek for the causes of capacity deterioration of  $\text{MnO}_2$  electrodes. Although Hol exhibits a very large discharge capacity, the capacity fading upon cycling is observed. The causes for such a behavior are estimated as; 1) Mg ion trapping in the host lattice, 2) leaching of Mn ions to electrolyte, and 3) unexpected presence of  $\text{ClO}_4^-$  in  $\text{MnO}_2$  tunnel from  $\text{Mg}(\text{ClO}_4)_2$  electrolyte, which can be regarded as one of the major reasons for structural instability of host structure.

In chapter 8, the conclusions and future prospects of the study are reported. The large specific capacity and high rate property of Hol composite material indicate this material to be a potential candidate for the electrode material of Mg-ion batteries, nevertheless further research work to improve the cyclic performance is essential. Moreover, modification of the residual ions ( $K^+$  and  $\text{H}_2\text{O}$ ) in the tunnel of  $\text{MnO}_2$  and optimization of the microstructural design of  $\text{MnO}_2$  composite is found to be very effective to control the electrode properties.