Cathodic Characteristics of Amorphous Manganese Oxides as Lithium Secondary Battery

H. Yagi*, T. Ichikawa*, A. Hirano**, N. Imanishi*, S. Ogawa* and Y. Takeda*
*Department of Chemistry, Faculty of Engineering, Mie University, Kamihamacho, Tsu, Mie 514-8507, Japan
**Laboratory of electron microscopy, school of medicine, Mie University, Kamihamacho, Tsu, Mie 514-8507, Japan

Abstract. The amorphous manganese dioxides were prepared by reduction method using various reagents. The particle size and morphology depended on reducing agents, some of which were aggregated round particles of sub micron order, and the others were small fine fibers like of a few nm in width and several tens nm in length. The former showed low Li-insertion capacity of around 200 mAhg⁻¹, while the latter material showed high capacity of 500 mAhg⁻¹ in the OCV measurements until 1 V vs. Li. The as-prepared MnO₂ contains some amount of water in the structure. The H₂O-free MnO₂ obtained by heat-treatment under high oxygen pressure was inferior in electrode property to MnO₂ containing water in the structure. The H₂O content related to the electrode performance.

1. Introduction
Since the lithium ion secondary battery began to be commercially produced, the cathode materials replaceable for LiCoO₂ have been extensively looked for. The spinel type LiMn₂O₄ system has just begun to be practically used. In these ten years, although the cyclability is not sufficient, the manganese dioxides themselves have been also focused as a candidate of cathode materials for a lithium secondary battery because of their low cost, safety and familiarity [1,2]. Moreover, they have potentially the larger capacity than conventional materials such as LiMn₂O₄ and LiCoO₂ that can use only half of the theoretical capacity to keep the performance. As shown in many references concerning their structural chemistry [1-3], "MnO₂" forms a large variety of crystalline structures consisting of various interlinking of MnO₆ octahedrons and interstitial spaces formed by the linkage. The stabilization of such variety-rich structures is due to the presence of various ions in the cavity as filler, such as K⁺, Na⁺, Li⁺, Ba²⁺ ions as well as protonic species. The performance as a cathode of lithium secondary battery has been reported for the various "MnO₂" species such as α-MnO₂ [4,5], β-MnO₂ [6], γ-MnO₂ [7], layer structure MnO₂[8] and so on. Some of them show the fairly high capacity of 200 mAhg⁻¹ but insufficient for the cycle performance. The subtle different situations of the included alkaline and protonic ions in the structure may strongly affect the electrode performances.

In the previous paper, we reported the cathode performances of the amorphous precipitates obtained by the reduction of permanganates. Some of them showed high capacity of more than 200 mAhg⁻¹ in a first few cycles and kept the capacity of 150 mAhg⁻¹ for a long cycle [9]. In this paper, the amorphous precipitates were heat-treated under high oxygen pressure in order to control the water content in the structure. The effect of included water on the cathode performance is reported.

2. Experimental Aspects
3 g-KMnO₄ was solved in 600 ml distilled water and reduced by reagents such as HCOOH and H₂O₂ (KMnO₄: reagents = ca 1:1.5). The aqueous solution or powder of
the reducing agent was added little by little in the stirred permanganate solution. In some cases, NH₄Cl was added before reduction aiming the insertion of NH₄⁺ ions in the structure. Then the precipitates were washed with water for several times, and dried at 300 °C for 1 hour in air.

Additionally, some powder of the derived MnO₂ prepared with HCOOH as a reducing agent (shown as MnO₂(HCOOH)) were treated at 300-500 °C for 24 h under 100 atm of oxygen gas to remove proton or H₂O from the structure.

To obtain the information on crystal structures, measurements by X-ray diffraction (XRD, Rigaku RAD-RC (12kW)) and high-resolution transmission electron microscopy (HRTEM, Hitachi, H-9000) were performed. Thermogravimetric analysis was measured using RIGAKU TG-8120.

To test the charge-discharge performance as a cathode, a conventional Li coin type cell was assembled. The sample (50 mg) was ground and mixed with acetylene black (shown as A.B., 10 mg) as an electron conductor and Teflon (0.5 mg) as a binder and the mixture was pressed into a tablet of 12 mm in diameter under a pressure of 1 MPa. The cell was assembled using this tablet as a cathode, Li sheet as an anode, Celgard© as a separator film and 1 M LiClO₄/ethylene carbonate (EC)+1,2-dimethoxycarbonate (DMC) as the electrolyte. Most of the Charge-discharge measurements were carried out in the range of 3.9-2.0 V with the current density of 0.2 mA/cm².

3. Results and Discussion

3.1. Influence of Reducing Agents and Microstructure on Charge-Discharge Properties. Figure 1 shows the high-resolution TEM (HRTEM) images for the "MnO₂" prepared from different reducing agents. The particle shapes and sizes depend on the agents used. When mild reducing agent H₂O₂ is used, aggregated particles of around 100 nm are mainly observed, while fiber like fine particles (a few nm in diameter) are predominant in both cases of H₂O₂ with NH₄Cl and HCOOH. The crystal structures of MnO₂ range over various types of polymorph such as tunnel or layer structures. Although it is difficult to determine the structure from TEM images, it is presumed that all MnO₂ samples mainly consist of birnessite from the information of lattice interval in XRD patterns [9].

Figure 2 shows the first discharge curves for the "MnO₂" precipitates (dried at 300 °C) obtained from various reducing agents. The correlation between particle