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STRUCTURAL PHASE TRANSITION AND ELECTRODE CHARACTERISTICS OF $LiMn_{2-x}Mg_xO_4$ POSITIVE ELECTRODE MATERIAL FOR THE LITHIUM SECONDARY BATTERY

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ABSTRACT

With in mind improving the cycle performance of 4V class lithium manganese oxide positive electrode material for the lithium secondary battery, we have been investigated the effects of partial substitution of Mn by another metal. The crystal phase transition in the quaternary spinel $LiMn_{2-x}Mg_xO_4$ was studied by neutron powder diffraction at 200K and DSC measurements at low temperatures. We find that substituting Mn by Mg resulted in a more stable crystal structure with the Jahn-Teller transition suppressed down to low temperature. The charge-discharge characteristics of these positive electrode active materials were investigated at 4V range. Although the discharge capacity decreased with increasing Mg content, the cycle performance was improved with increasing Mg content.

INTRODUCTION

The utilization of stoichiometric lithium manganese oxide as positive electrode material for the lithium secondary battery has been shown to exhibit poor cycling behavior. Yamada et al. reported a first-order Jahn-Teller structural phase transition of $LiMn_2O_4$ from cubic to tetragonal symmetry at around 280K (1). They also reported a suppression of the Jahn-Teller distortion by excess substitution of Mn with Li. Another approach to overcome these problems is to partially replace Mn by other transition metals, yielding $LiMn_{2-x}M_xO_4$(M = Co, Cr, Ni, Cu, Ti, Ge, Fe, Zn, Ga, Mg, V) (2)-(14), and $LiM_{\delta/2}Mn_{2-\delta}O_4$. (15). We have prepared a single-phase quaternary spinel $LiMn_{2-x}Mg_xO_4$ for x=0-0.2. The lattice parameter ***a*** decreases and the Mn valence increases with increasing Mg content. Partial substitution Mn with Mg improves the cycling performance in spite of some decrease of the initial capacity (16). The Jahn-Teller distortion is expected to occur at a temperature lower than that of $LiMn_2O_4$ because Mg^{2+} doping leads to a decrease of Mn^{3+} ions in the metal.

In this paper, we report the studies of the crystal phases and the electrochemical properties of $LiMn_{2x}Mg_xO_4$ by neutron powder diffraction, DSC measurements, and charge-discharge characterization.