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Improvement of lithium-containing manganese dioxide (composite dimensional manganese oxide: CDMO) as positive material for lithium secondary batteries

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Abstract

Lithium-containing manganese dioxide (CDMO) has been developed as the positive material for lithium secondary batteries. CDMO is prepared from lithium salt and manganese dioxide by heat treatment. The material is a composite oxide of γ/β-MnO_2 and Li_2MnO_3. The charge condition has been investigated in order to develop an improved CDMO that will exhibit a higher discharge voltage and a larger capacity. CDMO charged to a high potential (i.e., 3.6 V versus Li–Al electrode) displays higher discharge voltage and larger capacity than CDMO subjected to normal charge (i.e., 3.3 V versus Li–Al). It is concluded that when CDMO is charged to a high potential, lithium inserted not only by electrochemical reaction but also by heat treatment are removed from the γ/β-MnO_2 phase. The optimum conditions for preparing improved CDMO is to heat treat LiOH and electrolytic manganese dioxide (EMD) at a Li/Li+Mn atomic ratio of 0.3 at ~250 °C. The improved CDMO delivers a discharge capacity of over 200 mA h g^{-1}. Also, excellent rechargeability is experienced, even when CDMO is charged to a high potential.

Introduction

The demand for a secondary battery with high energy density has increased with the advancement of electronic devices. As a result, the research and development of secondary lithium batteries have been intensified. In the work reported here, a high-voltage, inexpensive lithium secondary battery has been investigated using MnO_2 as the positive material. It has been reported that MnO_2 has poor rechargeability [1, 2]. In order to overcome this problem, lithium-containing manganese dioxide has been prepared from lithium salt and MnO_2. This material is a composite oxide of γ/β-MnO_2 and Li_2MnO_3 (composite dimensional manganese oxide: CDMO). The crystal structure, cycling performance and optimum preparation method for CDMO has been reported previously [3, 4]. CDMO exhibits superior performance to γ/β-MnO_2 and spinel $LiMn_2O_4$. The optimum condition for preparing CDMO is to heat treat LiOH and MnO_2 at about 375 °C. CDMO prepared from sodium-free EMD (electrolytic manganese dioxide) exhibits superior discharge capacity. This paper discusses a study aimed at the development of an improved CDMO that will exhibit higher discharge voltage and greater capacity.

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