Thermal stability of high voltage spinel with disordered and ordered phase

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Introduction

High voltage spinel $LiNi_xMn_{2-x}O_4$ (x is around 0.5 and will be referred to as LNMO) has been heavily investigated recently due to its advantage of high operating voltage at ~4.7V versus Li^+/Li[1]. Its electrochemical performance has been shown to depend on many factors, including synthesis route, stoichiometry, heat treatment, morphology and particle size[2]. In order to improve the electrochemical performance of this cathode material, the studies of structural stability are important. The delithiated form of its parental material, $LiMn_2O_4$, has been investigated by Dahn and his research group extensively. They showed that chemically delithiated $LiMn_2O_4$ transforms from λ-MnO_2 to β-MnO_2 at 270°C and further decomposes to α-Mn_2O_3 at 550°C. This is in good agreement with the theoretical calculation reported later. Since there is no oxygen release until above 500°C, $LiMn_2O_4$ is generally regarded as a relatively safe cathode material compared with layer structured materials[3]. However, when one quarter of total Mn is replaced by Ni as in LNMO, it was found in this study that the thermodynamics of LNMO and its structural stability are quite different from those of regular spinel $LiMn_2O_4$.

DSC measurement of delithiated LNMO has been examined by Patoux and Chen[4]. They both observed exothermic peaks around 250°C. Bhaskar et al investigated substituted spinel $Li_{1-\Delta}M_{0.5}Mn_{1.5}O_4$ (M = Fe, Co, Ni) and compared thermal stabilities of these materials with different substituted transition metals. To our best knowledge so far, the reaction mechanism of delithiated LNMO at elevated temperature has not been systematically studied.

In this work, we applied synchrotron-based *in situ* tools to monitor changes in both crystal- and electronic-structure to study the reaction mechanism of delithiated LNMO during heating. By making comparison between ordered and disordered LNMO, we have studied the origin of difference in their thermal and structural stabilities from thermo dynamical perspectives.

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