

Boron-doped $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ as a cathode active material for lithium ion battery



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ABSTRACT

Lithium-rich manganese-based layered oxide material, $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$, was successfully synthesized via a solid-state method, and its structural and electrochemical properties were compared with the boron-doped $\text{Li}_{1.2}\text{Mn}_{0.6-x/2}\text{Ni}_{0.2-x/2}\text{B}_{x/2}\text{O}_2$ ($x = 0, 0.02$ and 0.04) cathode materials. The structure and morphology of the cathode samples have been investigated by X-ray powder diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). The electrochemical properties of cathode materials have been characterized systematically with different electrochemical techniques. According to XRD and SEM results crystallite size of materials increase with increasing boron content. Boron doping exhibits remarkable improvement in capacity, cyclability and rate capability compared to bare $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$. The initial charge and discharge capacities at 0.1C rate were observed at 318 and 253 mAh g^{-1} for $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$, 318 and 239 mAh g^{-1} boron-doped materials, respectively. In addition, the boron-doped cathode exhibits a long-term cycling stability with the capacity fade of only 12% after 275 cycles at 1C current discharge rate. However, the addition of more boron does not have an extra electrochemical performance.

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1. Introduction

Lithium ion batteries are becoming the main power sources of various applications due to their various advantages, including higher energy density and longer cycle life than other commercial battery technologies. Lithium cobalt oxide (LiCoO_2) was the first investigated layered structure active materials for positive electrode that was commercialized in 1991 [1]. Today's commercialized positive electrode materials can be described three classes of crystal chemistry: layered oxide (LiMO_2), spinel oxide (LiMn_2O_4), and olivine phosphate (LiMPO_4), ($M = 3d$ transition metals such as Co, Mn, Fe, Ni, etc.) [2,3]. Although LiCoO_2 is a successful and most commonly used cathode material in lithium ion batteries, many efforts have been progressed to find alternative cathode materials, which are the key active component of the battery to be improved in terms of energy and power density, stability and safety [4–6]. Recently, the layered Li-excess nickel manganese oxide $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Co, Ni, Mn, etc.}$) has attracted much attention as the most promising cathode candidates for high energy lithium ion batteries because of its high specific capacity ($>200 \text{ mAh g}^{-1}$) and high average operating potential ($>3 \text{ V}$) and low cost [8–11]. Thackeray et al. have reported that more than one Li ion per formula unit can be extracted from a solid solution of $\text{Li}_2\text{MnO}_3 \cdot \text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ and thus delivered above 250 mAh g^{-1} capacity [8].

Although these layered structures are one of the most promising candidates for heavy-duty applications such as hybrid and electric vehicles,

some disadvantages such as large irreversible capacity loss, voltage instability and poor rate capability prevent their application [8–11]. The irreversible capacity loss in the first charging process mainly takes place at the starting part of the long oxygen release plateau above 4.5 V. The rearrangements of the crystal structure of the Li-rich materials have been shown that the reason of the irreversible capacity loss [8–13]. Much complex transition metal arrangements have not been explained in detail. Some recent researches give evidence suggesting a second phase appearing at high voltage region [13]. The long charge plateau disappears after the initial cycle, suggesting that the structural changes in the bulk mainly take place during the first charge. The layered to spinel transformation has long been postulated as an important factor to account for the capacity fading and poor rate performance of the layered structure materials [14–21]. It has not exactly been understood where the spinel phase nucleates and how the spinel phase grows during charge-discharge process of the layered structured phase.

Tang et al., investigated Co doping effect on Li-rich Mn-based cathode materials. They conclude that Co doping makes the particle size grows more homogeneously and Co-doped samples express the highest initial efficiency and the highest energy density compared to non-doped samples [22]. Wang and Manthiram reported a systematic investigation of substitution of various ions (such as Al^{+3} , Cr^{+3} , Fe^{+3} , Co^{+3} , Ga^{+3} , Ti^{+4} and Mg^{+2}). They showed that the discharge capacity values in subsequent cycles decreases in the order $\text{Co} > \text{pristine} > \text{Fe} > \text{Al} > \text{Cr} > \text{Ga}$ for $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ sample [23]. Fe-doped layered $\text{Li}_{1.2}\text{Mn}_{0.6-x/2}\text{Ni}_{0.2-x/2}\text{Fe}_{x/2}\text{O}_2$ cathode materials investigated and $\text{Li}_{1.2}\text{Mn}_{0.585}\text{Ni}_{0.185}\text{Fe}_{0.03}\text{O}_2$ showed best performance as a cathode material [24]. In our previous

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work, a nanosized layered $\text{Li}(\text{Li}_{0.1}\text{Ni}_{0.3}\text{Mn}_{0.5}\text{Fe}_{0.1})\text{O}_2$ cathode active material was successfully synthesized by solid-state method and the initial capacity was observed 205 mAh g^{-1} [25]. In the literature, there are some data on the use of new cathode materials based on LiCoO_2 [26,27], LiV_3O_8 [28] and LiMn_2O_4 [29] with boron additive. The boron doping

stabilizes the cathode materials and improves the electrochemical performance [26–29].

It is thought that boron addition should improve electrochemical properties of lithium-rich layered cathode materials. For this purpose, $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ is one of the promising cathode material for practical

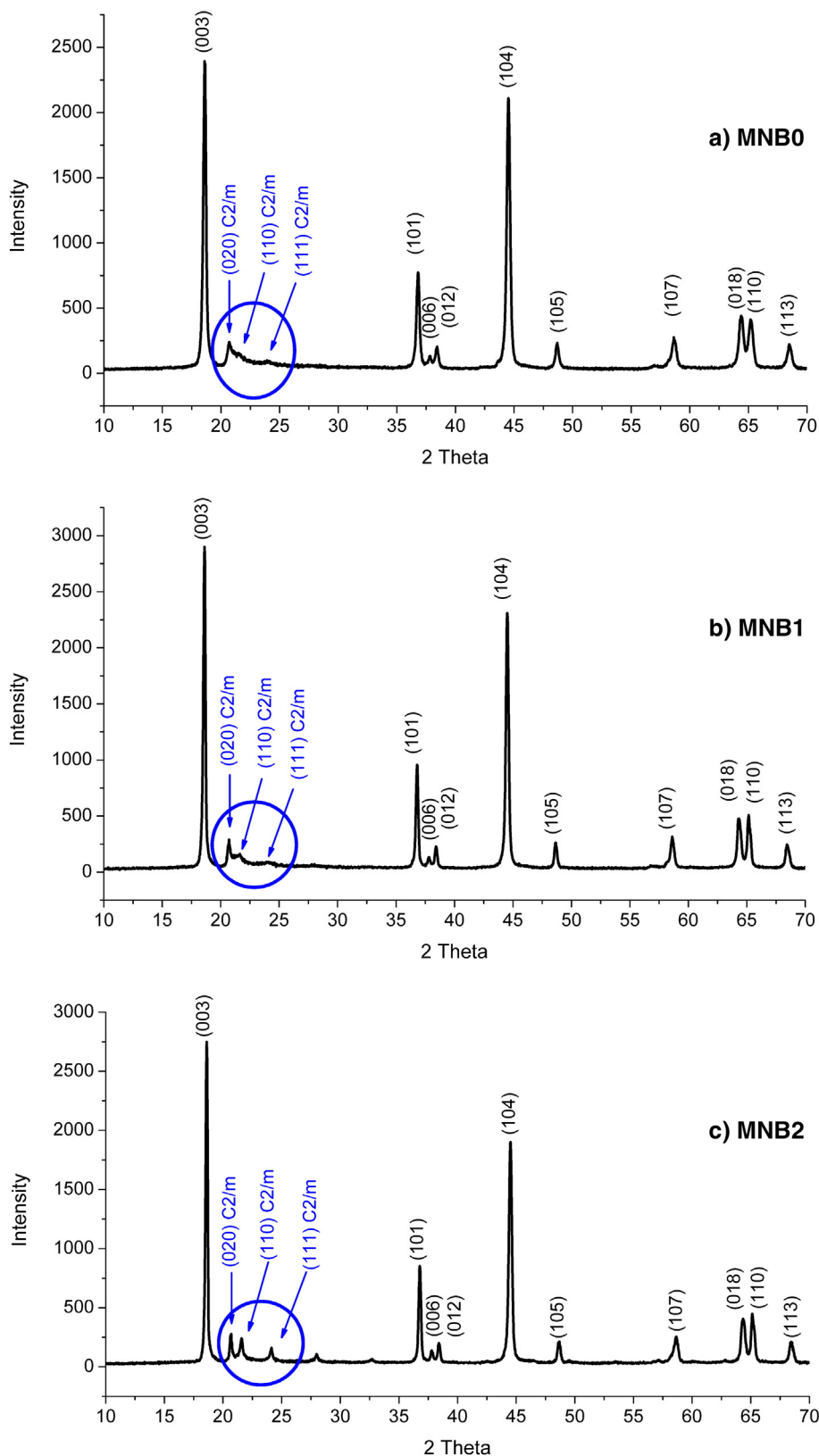


Fig. 1. X-Ray diffraction patterns of MNB0, MNB1 and MNB2 cathode materials.

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