

Orthorhombic $\text{LiCo}_x\text{Mn}_{1-x}\text{O}_2$ ($0 \leq x \leq 0.2$) as Cathode Materials for Lithium-Ion Batteries

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Orthorhombic LiMnO_2 (hereafter referred as to $o\text{-LiMnO}_2$) having a zig-zag layered structure (space group $Pnmm$) is an attractive alternative to spinel LiMn_2O_4 oxide as a cathode material in lithium-ion secondary batteries. Because the LiMnO_2 gives a twice of theoretical capacity (285 mAh g^{-1}) of LiMn_2O_4 based on electrochemical reaction of $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple. Though it offers a relative higher capacity, there is a problem of this material, that is, difficulty of synthesis. Some of earlier researchers have tried to prepare $o\text{-LiMnO}_2$ having a high capacity, but the cyclability was still remained unsolved. In previous researches, low temperature preparation seemed to have a beneficial effect to obtain higher capacity.

Jang et al. [1] reported a good cyclability of $o\text{-LiMnO}_2$ having high capacity with help of high temperature calcination around 950°C of freeze dried precursor which has very homogeneous mixed cations. But, this method needs careful control of oxygen partial pressure during calcination. If not, unwanted impurity phases are contained.

To simplify powder preparation, hydrothermal reaction is very attractive method to synthesize $o\text{-LiMnO}_2$ at relatively low temperature [2]. Recently, we have successfully prepared $o\text{-LiMnO}_2$ hydrothermally from Mn_3O_4 and LiOH at 170°C [3]. The $o\text{-LiMnO}_2$ demonstrated high capacity ($> 200 \text{ mAh g}^{-1}$) as well as a good cyclability in Li cell. In the case, there is no need to control the oxygen partial pressure carefully in preparation. Furthermore, there are few reports dealing with $o\text{-LiMnO}_2$ substitution by other transition elements to our knowledge. In fact, when some part of manganese sites is replaced by other elements (Al, Cr), monoclinic LiMnO_2 (hereafter referred as to $m\text{-LiMnO}_2$) structure was formed [5,6]. Here, we have succeeded to substitute a part of the manganese site with Co by hydrothermal treatment of Co doped Mn_3O_4 [4] at 170°C .

The synthesized $(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$ ($0 \leq x \leq 0.5$) were hydrothermally treated with 3.5 mol dm^{-3} LiOH aqueous solution at 170°C for 4 days [3].

During hydrothermal reaction in LiOH aqueous solution, the $(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$ ($0 \leq x \leq 0.5$) phases were gradually changed to orthorhombic phase. According to XRD patterns where all peaks can be indexed as $o\text{-LiMnO}_2$, solid solution can be formed up to $x = 0.2$ in $\text{LiCo}_x\text{Mn}_{1-x}\text{O}_2$.

As shown clearly in Fig. 1, higher as well as stable discharge capacities over 100 cycles were obtained in Co doped cell. It is reasonable to think that the transformation of $o\text{-LiMnO}_2$ to spinel would progressively occur much faster than undoped one, since the stronger bonding Co-O than Mn-O in octahedron environment can supply much

more stabilized spinel-like structure. That may lead to much more enhanced cyclability in a long term. These results suggest that the Co doped $o\text{-LiMnO}_2$ having high capacity retention upon cycling is more stable to cycle than the unsubstituted material.

Furthermore, we tried the synthesis of $o\text{-LiMnO}_2$ by calcination of the emulsion-dried precursor [7] at 925°C . Compared to the hydrothermal synthesis, the emulsion drying method was advantageous to obtain high capacity upon cycling.

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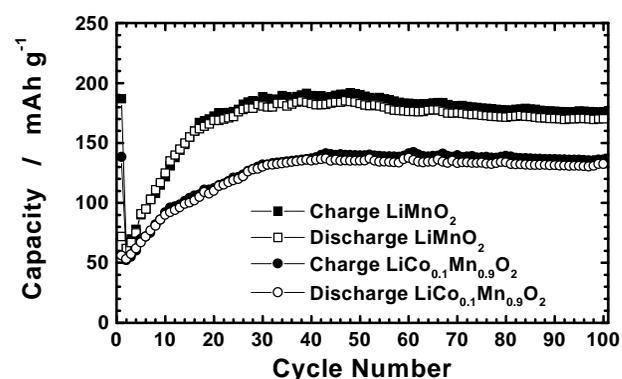


Figure 1. Charge-discharge capacities of $o\text{-LiCo}_x\text{Mn}_{1-x}\text{O}_2$ ($x = 0, 0.1$) synthesized by hydrothermal treatment at 170°C . An applied current density was 0.1 mA cm^{-2} in $1 \text{ M LiClO}_4 \text{ EC:DEC (1:1)}$ at 25°C .

References

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