

Synthesis and characterization of $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ as the cathode materials of secondary lithium batteries

Zhaolin Liu^{a,*}, Aishui Yu^a, Jim Y. Lee^b

^a Institute of Materials Research and Engineering (IMRE), University of Singapore, Singapore

^b Department of Chemical Engineering, National University of Singapore, Singapore

Abstract

$\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ ($0 \leq x \leq 0.5$, $0 \leq y \leq 0.3$) were prepared by heating $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y(\text{OH})_2$ and LiNO_3 in flowing oxygen for 10 h at 550°C, followed by another heating at 750°C. The XRD patterns of $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ ($0 \leq x \leq 0.5$, $0 \leq y \leq 0.3$) samples with different x and y values show a pure phase of layered hexagonal structure. The lattice parameters a , c and the unit cell volume are found to decrease with increasing x in $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$. The partial substitution of Ni by Co and Mn as in $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ and $\text{LiNi}_{1-y}\text{Co}_{0.2}\text{Mn}_y\text{O}_2$ has a positive effect on lithium stoichiometry. However, lithium deficiency is still found after a prolonged thermal treatments (24 h). Among the doped materials synthesized, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ have shown the best characteristics in terms of initial capacity and cycle life. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Secondary lithium cell; Lithium nickelate–cobalt and manganese substituted; Cathode materials

1. Introduction

LiNiO_2 is one of the most promising cathode materials for secondary-lithium cells. The main advantages of LiNiO_2 are its low cost (compared to LiCoO_2), and the possibility of a higher charge/discharge capacity. However, charging must be carefully controlled as over de-lithiation easily occurs, resulting in structural changes that can cause a substantial decrease in the discharge capacity [1]. Stoichiometric LiNiO_2 is difficult to synthesize and lithium deficient $\text{Li}_a\text{Ni}_{2-a}\text{O}_2$ ($0 < a < 1$) compounds are formed instead in most common preparations [2–5]. Oxidation difficulty in converting Ni^{2+} to Ni^{3+} appears to be the main reason [6]. The capacities of LiNiO_2 -based batteries also tend to deteriorate with cycling. This unsatisfactory material characteristics must be overcome before LiNiO_2 can become a serious contender to replace LiCoO_2 in rechargeable lithium-ion batteries. Solid solutions of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ($0 \leq x \leq 1$) have been suggested as an alternative to LiNiO_2 because the structural instability of the latter can be reduced in the presence of Co [7,8]. Although high cobalt doping ($x \geq 0.3$) is reported to be necessary for cycle stability, replacement of Ni by the

more expensive Co also adds to the cost of material synthesis. There are also attempts on the partial replacement of the nickel ions in LiNiO_2 by manganese ions giving rise to the $\text{LiNi}_z\text{Mn}_{1-z}\text{O}_2$ ($0.5 \leq z \leq 1$) series of compounds [9,10]. Some deterioration of the electrochemical properties of LiNiO_2 was found [9]. Nevertheless, the advantage of using a low cost component such as Mn can lead to substantial reduction in the production cost much below that of lithium–nickel–cobalt oxides. Studies on other mixed compounds such as $\text{LiCo}_z\text{Mn}_{1-z}\text{O}_2$ with $0 < z < 1$ [11] and $\text{LiNi}_x\text{Al}_{1-x}\text{O}_2$ with $0.7 \leq z \leq 1$ [12] have also been reported. In this paper, we report a successful preparation of $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ ($0 \leq x \leq 0.5$, $0 \leq y \leq 0.3$) using $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y(\text{OH})_2$ and LiNO_3 as the starting materials. The crystal structure and the electrochemical characteristics of these materials were also investigated.

2. Experimental

$\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ ($0 \leq x \leq 0.5$, $0 \leq y \leq 0.3$) were prepared using $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y(\text{OH})_2$ and LiNO_3 as the starting materials. $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y(\text{OH})_2$ were in turns synthesized as follows: known amounts of NiSO_4 , CoSO_4 and MnSO_4 were dissolved in distilled water. The mixed

* Corresponding author. Fax: 65-8720785; E-mail: zl-liu@imre.org.sg

Table 1

Lattice parameter and volume of the $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ unit cell and the intensity ratio $I(003)/I(104)$

Composition	Formula determined by ICP-AES	a (Å)	c (Å)	Volume (Å) ³	Intensity ratio of $I(003)/I(104)$
LiNiO_2	$\text{Li}_{0.92}\text{Ni}_{1.08}\text{O}_2$	2.901	14.216	103.6	1.08
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	$\text{Li}_{0.96}(\text{Ni}_{0.80}\text{Co}_{0.20})_{1.04}\text{O}_2$	2.895	14.182	102.9	1.21
$\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$	$\text{Li}_{1.00}(\text{Ni}_{0.49}\text{Co}_{0.51})_{1.00}\text{O}_2$	2.886	14.141	102.0	1.44
$\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$	$\text{Li}_{0.94}(\text{Ni}_{0.70}\text{Co}_{0.20}\text{Mn}_{0.10})_{1.06}\text{O}_2$	2.876	14.093	101.0	1.13
$\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$	$\text{Li}_{0.96}(\text{Ni}_{0.61}\text{Co}_{0.19}\text{Mn}_{0.20})_{1.04}\text{O}_2$	2.895	14.186	103.0	1.40
$\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$	$\text{Li}_{0.98}(\text{Ni}_{0.50}\text{Co}_{0.20}\text{Mn}_{0.30})_{1.02}\text{O}_2$	2.908	14.250	104.4	1.50

Table 2

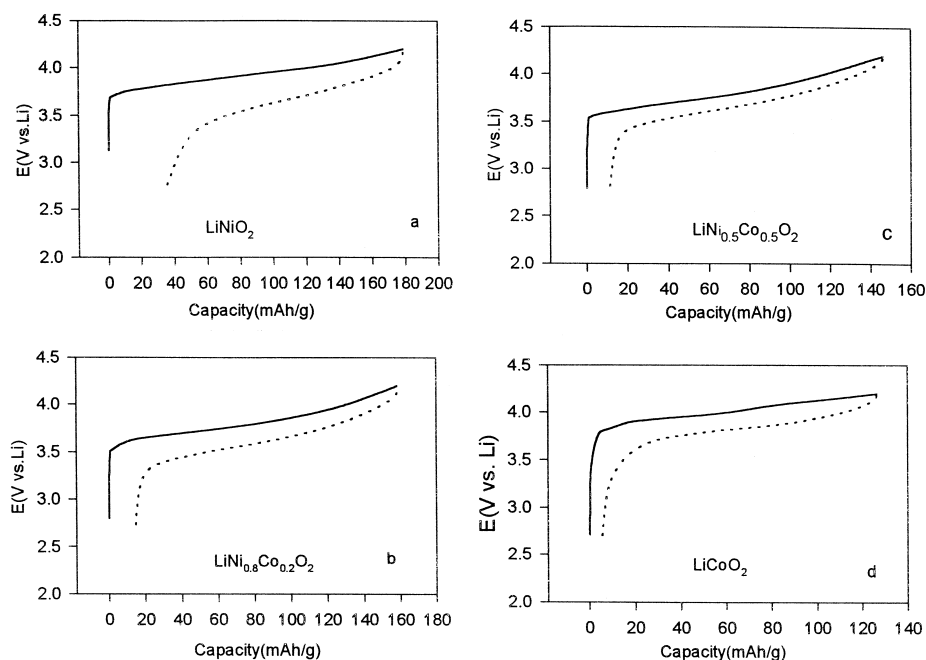
Effect of thermal treatment on composition

Expected formula	Formula determined by chemical analysis	
	750°C (24 h)	750°C (5 h)
LiNiO_2	$\text{Li}_{0.88}\text{Ni}_{1.12}\text{O}_2$	$\text{Li}_{0.92}\text{Ni}_{1.08}\text{O}_2$
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	$\text{Li}_{0.93}(\text{Ni}_{0.79}\text{Co}_{0.21})_{1.07}\text{O}_2$	$\text{Li}_{0.96}(\text{Ni}_{0.80}\text{Co}_{0.20})_{1.04}\text{O}_2$
$\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$	$\text{Li}_{0.98}(\text{Ni}_{0.50}\text{Co}_{0.50})_{1.02}\text{O}_2$	$\text{Li}_{1.00}(\text{Ni}_{0.49}\text{Co}_{0.51})_{1.00}\text{O}_2$
$\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$	$\text{Li}_{0.93}(\text{Ni}_{0.69}\text{Co}_{0.20}\text{Mn}_{0.11})_{1.07}\text{O}_2$	$\text{Li}_{0.94}(\text{Ni}_{0.70}\text{Co}_{0.20}\text{Mn}_{0.10})_{1.06}\text{O}_2$
$\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$	$\text{Li}_{0.95}(\text{Ni}_{0.60}\text{Co}_{0.19}\text{Mn}_{0.21})_{1.05}\text{O}_2$	$\text{Li}_{0.96}(\text{Ni}_{0.61}\text{Co}_{0.19}\text{Mn}_{0.20})_{1.04}\text{O}_2$
$\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$	$\text{Li}_{0.96}(\text{Ni}_{0.49}\text{Co}_{0.21}\text{Mn}_{0.30})_{1.04}\text{O}_2$	$\text{Li}_{0.98}(\text{Ni}_{0.50}\text{Co}_{0.20}\text{Mn}_{0.30})_{1.02}\text{O}_2$

The preparation was carried out in flowing O_2 (0.4 l/min).

solution was added to a stirred NaOH solution at ca. 60°C. The resulting slurry was filtered and washed to recover the precipitated $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y(\text{OH})_2$. After drying in air at 120°C for 8h, $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y(\text{OH})_2$ and LiNO_3 were grounded together and pelletized. The pellets were precalcined at 550°C for 10 h in flowing oxygen. The resulting black powder was grounded once more, and calcined at 750°C, again in flowing oxygen.

The samples were characterized by XRD using a Philips PW1877 automated powder diffractometer and $\text{CuK}\alpha$ radiation. Li, Ni, Co and Mn contents in terms x , y and a in the formula $\text{Li}_a(\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y)_{2-a}\text{O}_2$ were determined by ICP-AES (Inductive Coupling Plasma-Atomic Emission Spectroscopy) using the solutions of the quaternary oxides in HNO_3 . For the fabrication of working electrodes $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ was mixed with 10% of carbon

Fig. 1. The first charge and discharge curves of $\text{Li}/\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($x = 0, 0.2, 0.5, 1$) cells in 1 M $\text{LiPF}_6\text{-EC-DMC}$ (1:1) at a rate of $0.2 \text{ mA}/\text{cm}^2$.

black and 5% of polytetrafluoroethylene (PTFE) and coated onto thin Al disks. The electrodes were dried in vacuum at 120°C for 8h before use. Typical cathode loading was ca. 10 mg/cm² of active material. The electrolyte was a 1 M LiPF₆ solution in EC-DMC (1:1). Lithium pellets were used as both the reference and counter electrodes. All handling and fabrication were carried out in an argon-filled dry box.

3. Results and discussion

3.1. XRD characterization and chemical composition of LiNi_{1-x-y}Co_xMn_yO₂ samples

Over the entire composition range ($0 \leq x \leq 0.5$, $y = 0$), a pure phase of LiNi_{1-x}Co_xO₂ could be identified. The X-ray diffraction patterns of LiNi_{1-x}Co_xO₂ ($0 \leq x \leq 0.5$) are characteristic of that of α -NaFeO₂ in which the transition metal ions are surrounded by six oxygen atoms. Infinite layers of Ni_{1-x}Co_xO₂ were formed through edge-sharing of the (Ni_{1-x}Co_xO₆) octahedras, with the intercalating lithium ions located between the layers. All of the diffraction lines of LiNi_{1-y}Co_{0.2}Mn_yO₂ ($y = 0.1, 0.2, 0.3$) can be indexed with a hexagonal lattice. Table 1 gives the computed results of the lattice parameters of the hexagonal cell and the intensity ratio $I(003)/I(104)$.

As can be seen in Table 1, when the Ni³⁺ ions at the 3(a) sites of the LiNiO₂, lattice are partially replaced by Co³⁺ ions, the unit cell dimensions, a and c , in a hexagonal setting become smaller ranging from $a = 2.901 \text{ \AA}$ and $c = 14.216 \text{ \AA}$ for LiNiO₂ to $a = 2.886 \text{ \AA}$ and $c = 14.141 \text{ \AA}$ for LiNi_{0.5}Co_{0.5}O₂ due to the difference in size between trivalent cobalt and trivalent nickel ions ($r_{\text{Ni}^{3+}} = 0.56 \text{ \AA}$, $r_{\text{Co}^{3+}} = 0.53 \text{ \AA}$) [13]. These results suggest that LiNi_{1-x}Co_xO₂ ($0 \leq x \leq 0.5$) is a homogeneous phase, with Ni³⁺ and Co³⁺ ions occupying the octahedral 3(a) sites of a cubic-close packed oxygen array. On the other hand, with manganese doping in LiNi_{1-y}Co_{0.2}Mn_yO₂ ($y = 0.1, 0.2, 0.3$), the unit cell dimensions a and c have become larger following the increase in y .

The results of chemical analyses for LiNi_{1-x}Co_xO₂ ($0 \leq x \leq 0.5$) and LiNi_{1-y}Co_{0.2}Mn_yO₂ ($y = 0.1, 0.2, 0.3$) are shown in Table 2. The results clearly indicate the positive effect of Co and Mn substitution for Ni on lithium stoichiometry. Subsequently, the number of Ni²⁺ ions at the 3a sites is reduced, easing the cationic disorder in the lithium layers. The Ni/Co ratio measured by chemical analysis is in good agreement with the initial ratio in the mixture. Lithium deficiency is a lesser problem for short thermal treatment (5 h). With the increase in the time of thermal treatment, lithium evaporation as Li₂O from LiNi_{1-x-y}Co_xMn_yO₂ occurs, leading to products of reduced Li contents.

3.2. Electrochemical characteristics of LiNi_{1-x-y}Co_xMn_yO₂ samples

Figs. 1 and 2 show the charge and discharge curves of LiNi_{1-x}Co_xO₂ ($0 \leq x \leq 0.5$, $x = 1$) and LiNi_{1-y}Co_{0.2}Mn_yO₂ ($y = 0.1, 0.2, 0.3$) in nonaqueous lithium cells. Lithium metal was used as the anode. The reversible specific capacity of LiCoO₂ was limited to 120 mAh/g, and that of LiNiO₂ was around 155 mAh/g. One can immediately see the decrease in the specific capacities of the quaternary oxides LiNi_{1-x}Co_xO₂ ($0 \leq x \leq 0.5$) when the cobalt content in them (x) increases. When x reaches 0.2 and 0.5, the specific capacities are reduced to 144 mAh/g and 135 mAh/g, respectively. The high Ni content samples have increased capacities but lower (average) discharge potentials compared to the Co rich samples, indicating a greater extent of Li⁺ ions de-intercalation in the former. From the variation in electrode potential in the first charge/discharge cycle (Fig. 2), the introduction of

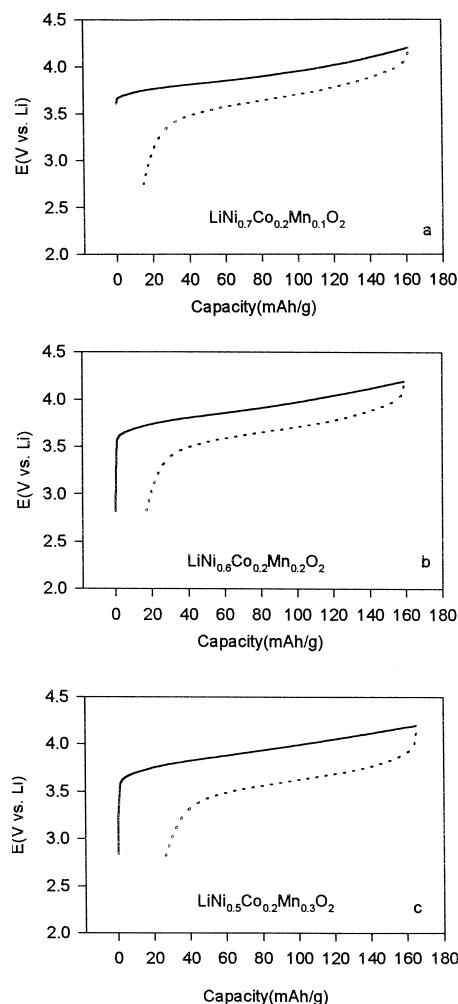


Fig. 2. The first charge and discharge curves of Li/LiNi_{1-y}Co_{0.2}Mn_yO₂ ($y = 0.1, 0.2, 0.3$) cells in 1 M LiPF₆-EC-DMC(1:1) at a rate of 0.2 mA/cm².

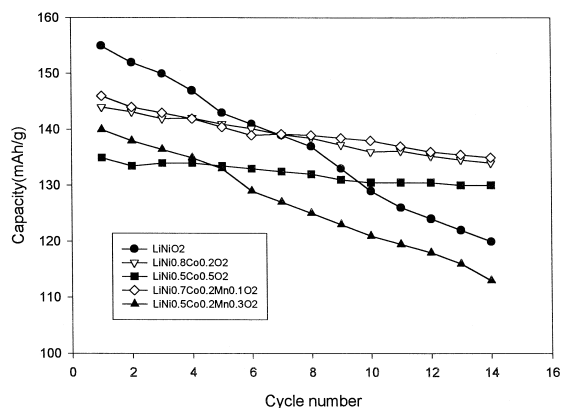


Fig. 3. Charge and discharge cycle performance of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($x = 0, 0.2, 0.5$) and $\text{LiNi}_{1-y}\text{Co}_{0.2}\text{Mn}_y\text{O}_2$ ($y = 0.1, 0.3$) (current density: 0.2 mA/cm^2 , voltage: $4.2\text{--}2.75 \text{ V}$ vs. Li).

Co has improved the reversibility of the intercalation, amidst some loss of capacity. There is also a noticeable decrease in discharge capacities of $\text{LiNi}_{1-y}\text{Co}_{0.2}\text{Mn}_y\text{O}_2$ ($y = 0.1, 0.2, 0.3$) with the extent of manganese doping, although the decrease might not be significant when y is smaller than 0.3 (Fig. 2). However, when the amount of Mn in $\text{LiNi}_{1-y}\text{Co}_{0.2}\text{Mn}_y\text{O}_2$ reaches 0.3, the decrease in the capacities of the active materials are rather substantial. This is probably due to the decrease in Li ion mobility caused by lattice distortions, disintegration of the crystal structure and imbalances in the mixed valence state.

Fig. 3 shows the cycle performance of LiNiO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$, $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$. Good cycling characteristics are possible with $x = 0.2$ and $x = 0.5$, although the initial capacity in the latter tends to be lower. Among the Mn doped samples, $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ shows good capacity and suppressed capacity loss upon cycling. Excess Mn doping as in the case of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ is inadvisable, as it induces as large a capacity loss on cycling as LiNiO_2 , which is known for its poor cycling behaviour, although its initial capacity is the highest (at 150 mAh/g).

Charged $\text{LiNi}_{1-y}\text{Mn}_y\text{O}_2$ is constituted differently from charged LiNiO_2 , as shown by their difference in electronic conductivity. There are reports on the considerable progress in these material aspects recently [14]. Cobalt and manganese doping should bring about a high mixed conductivity. The increase in polarization observed at the end of discharge is the result of re-intercalation difficulty caused by low ionic conductivity when most of the available sites are occupied. Cobalt and manganese substitution can lead to a decrease in the non-stoichiometric character of lithium nickelate. These are favorable factors leading to improved cycling characteristics.

4. Conclusions

$\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ ($0 \leq x \leq 0.5, 0 \leq y \leq 0.3$) were prepared by heating $\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y(\text{OH})_2$ and LiNO_3 in flowing oxygen for 10 h at 550°C , followed by further heating at 750°C . The XRD patterns of $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ ($0 \leq x \leq 0.5, 0 \leq y \leq 0.3$) samples with different x and y values show an homogeneous phase of a layered hexagonal structure without any impurity. The lattice parameters a , c and the unit cell volume are found to become smaller when trivalent nickel ions are partially substituted for trivalent cobalt ions in LiNiO_2 . On the contrary, manganese doping in $\text{LiNi}_{1-y}\text{Co}_{0.2}\text{Mn}_y\text{O}_2$ ($y = 0.1, 0.2, 0.3$) brings about the increase in the unit cell dimensions a and c large as y increases. The partial substitution of Ni by Co and Mn as in $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ and $\text{LiNi}_{1-y}\text{Co}_{0.2}\text{Mn}_y\text{O}_2$ has a positive effect on the maintenance of lithium stoichiometry. However, lithium deficiency is still noticeable if extended thermal treatments (24 h) are used in the synthesis. Compared to pure LiNiO_2 cells, cells that are constituted from $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ where x is 0.2 or 0.5 show improved cycling characteristics, although the initial capacity when $x = 0.5$ is substantially lower. $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ is also a material of good capacity and cycle life but excessive Mn doping as in the case of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ returns a cycle life as poor as that of pristine LiNiO_2 .

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