

Electrochemical performance of layered $\text{Li}[\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x]\text{O}_2$ cathode materials synthesized by a sol–gel method

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Abstract

Synthesis and characterization of $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ ($1/3 \leq x \leq 1/2$) electrode powders prepared by a sol–gel method were investigated. The synthesized $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ materials with single phase and $R\bar{3}m$ layered structure were confirmed from X-ray diffraction analysis. The particle size distribution of the materials synthesized by the sol–gel process is quite uniform. Increasing the x value in the synthesized $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ powder leads to decrease its particle size and increase its cation mixing. The average particle size for the $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ powder was found to be an order of 0.3–0.4 μm . The best specific capacity of 192 mAh g^{-1} was obtained for the $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ electrode with good capacity retention among the synthesized materials cycled at 0.1C in the potential between 3.0 and 4.5 V at room temperature. Although structural parameters of the $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ powder are similar to those of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder, its specific capacity is higher due to the increase of the stoichiometry of active site Ni. The increase of Ni and Mn content could reduce cost of the materials. It was found that the cell performance of the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ electrode drops dramatically and its cation mixing increases while the x value is higher than 0.4.

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1. Introduction

Layered LiNiO_2 and their derivatives are promising cathode material for lithium-ion batteries due to their high theoretical capacity and low cost [1–3]. However, the major problem associated with these electrodes is difficult to prepare a stoichiometric LiNiO_2 powders without cation mixing. Various approaches such as partial replacement of nickel by transition metals, changing preparation methods and conditions were adopted to improve its performance. The most appropriate and successful methodology is to improve the structural stability of LiNiO_2 electrode by partial replacement of Ni by Co and Mn ions [3–11]. A solution of $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ can be formed by the substitution of Ni ions by Co and Mn ions in LiNiO_2 . The introduction of Co in the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ electrode can eliminate its

cation mixing and enhance its structural stability by preventing phase transformation from layer to spinel and also improve its electrical conductivity [9]. However, increasing the content of Co in the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ electrode leads to increase its cost and reduce its specific capacity. On other hand, the electrochemically inactive Mn in the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ electrode also contributes for its structural stability and reduces its production cost. Ohzuku et al. and Hwang et al. have reported the specific capacity of around 150–200 mAh g^{-1} for the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials with a single phase and layered structure [5,6]. Dahn and co-workers have synthesized $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ electrode materials by a ‘mixed hydroxide’ method and they found that the cation mixing increases with the increase of Ni content in the synthesized materials [7,8]. The increase of low cost metals of Ni in $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ electrode could avoid electrolyte decomposition at the end of the charge potential and improve its initial specific capacity [5,11]. Furthermore, the increase of Mn can enhance its structural stability and reduce its

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production cost. However, the slightly higher content of cobalt ($0.1 \leq x \leq 0.3$) is necessary to achieve better cycle life, but the production cost increases with the increase of Co [3–8]. It is of great importance to optimize the cobalt content in the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ material to improve its electrochemical performance and reduce its cost simultaneously.

In order to improve their electrochemical properties and reduce their cost, an attempt to optimize the cobalt content in the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ ($1/3 \leq x \leq 1/2$) powders synthesized by a sol–gel process was performed. The structural properties, morphology and electrochemical properties of the synthesized $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ powders were investigated in the present work. The results were also compared with that of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode.

2. Experimental

Layered $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ ($1/3 \leq x \leq 1/2$) powders were synthesized by a sol–gel method using citric acid as a chelating agent. A stoichiometric amount of lithium acetate, manganese acetate, and nickel acetate and cobalt nitrate were chosen as starting materials to prepare the precursor. All the salts were dissolved in an appropriate quantity of distilled water and citric acid was added drop-wise with continuous stirring. After dissolution of all salts, the temperature of solution was raised to 80–90 °C and continued stirring till the clear viscous gel was formed. The gel was vacuum dried at 120 °C for 2 h to obtain the precursor powder. The precursor powder was decomposed at 450 °C in oxygen stream for 4 h and ground to fine powder and calcined at 900 °C for 12 h under oxygen flowing condition. The heating and cooling rate was maintained as 2 °C per minute.

The synthesized $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ ($1/3 \leq x \leq 1/2$) electrode powders were characterized by X-ray diffraction (Rikagu diffractometer, Rotaflex) using Cu K α radiation in the 2θ range of 10–80° with a scan rate of 2° per minute. The surface morphology and particle size distribution of the synthesized powders were examined by scanning electron microscopy (SEM) (JEOL, JSM 6500). Samples were prepared by gold sputtering on the surface of the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ powders. SEM images were obtained at an accelerating voltage of 15 kV with a magnification 10,000 \times .

Cathode films were prepared by mixing of active material, carbon black, KS6 graphite and polyvinylidene fluoride (PVdF) as a binder, respectively, in the ratio of 85:3.5:1.5:10 (w/w) and *N*-methyl pyrrolidinone (NMP) was used as a solvent. Slurry was obtained after mixing of carbon black, active material, PVdF binder with NMP solvent and stirring. The resulting slurry was cast on Al foil using a doctor blade. The coated Al foil was dried at 120 °C for 2 h to evaporate the NMP solvent. The coated foil was roll-pressed and punched to a circular disk. The electrode films were preserved in argon filled dry box (Unilab, MBrun).

Electrochemical measurements were performed on a coin type cell. The coin cell was assembled with

$\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ ($1/3 \leq x \leq 1/2$) as a cathode and the lithium (FMC) metal foil as an anode. A mixture of ethylene carbonate (EC): diethyl carbonate (DEC) (1:1) solvent containing 1 M LiPF_6 was used as an electrolyte. The polypropylene membrane was soaked in an electrolyte for 24 h prior to use. The coin cell was assembled in an argon-filled dry box in which the moisture and oxygen contents were maintained less than 1 ppm. The charge and discharge measurements were performed at 0.1C in the potential range of 3.0–4.5 V at room temperature.

3. Results and discussion

X-ray diffraction patterns of the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ ($1/3 \leq x \leq 1/2$) powders synthesized by treating the precursor at 900 °C for 12 h are shown in Fig. 1. The powders with a single phase and layered structure were confirmed from the XRD analysis. All the diffraction peaks were indexed based on the hexagonal structure, $\alpha\text{-NaFeO}_2$, with a space group of $R\bar{3}m$ in which the transition metal ions are surrounded by six oxygen atoms [3]. In the XRD pattern, the extra peaks around 20–25° are corresponding to the Vaseline. The lattice parameters (a and c) and the peak intensity ratio of $I_{(003)}/I_{(104)}$ were determined. Table 1 summarizes the calculated lattice parameters, c/a , and integrated intensity ratio. From Table 1, the lattice parameters such as $a = 2.873$ Å, $c = 14.29$ Å, $I_{(003)}/I_{(104)} = 1.37$ and $c/a = 4.97$ were obtained for $x = 0.375$. The slight increase in the lattice parameters with an increase in the x value is due to the difference in the size of the Ni^{2+} and Co^{3+} [4,8,12]. The value of $I_{(003)}/I_{(104)}$ is used to measure the degree of the cation mixing in the layered compounds. Smaller the $I_{(003)}/I_{(104)}$ value, the higher the disordering. If $I_{(003)}/I_{(104)}$ value is less than 1.2, it means that undesirable cation mixing takes place [5]. The $I_{(003)}/I_{(104)}$ value of 1.36 and 1.37 for the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ materials, respectively, indicating no undesirable cation mixing is observed in these two samples. However, the cation mixing is found if the cobalt content

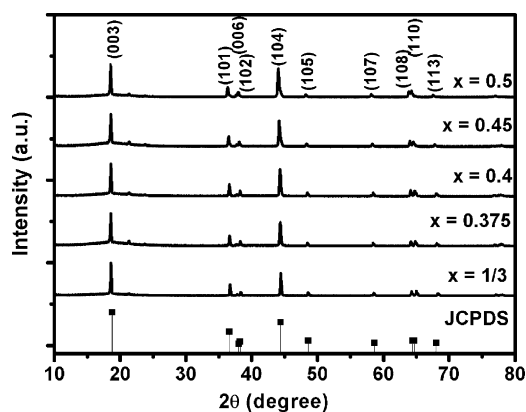


Fig. 1. X-ray diffraction patterns for $x = 1/3, 0.375, 0.4, 0.45, 0.5$ in $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$.

Table 1
Structural parameters of the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ system

$\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$	a (Å)	c (Å)	c/a	I_{003}/I_{104} (observed)	I_{003}/I_{104} (calculated)
$x=0.333$ (1/3)	2.866	14.27	4.98	1.36	1.393
$x=0.375$	2.873	14.29	4.97	1.37	1.382
$x=0.4$	2.876	14.293	4.97	1.20	1.381
$x=0.45$	2.885	14.296	4.96	1.26	1.376
$x=0.5$	2.897	14.321	4.94	1.14	1.364

in the synthesized materials is less than 0.2. The structural parameters of the $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ compound are similar to those of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ one.

The surface morphology of the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ electrode powders for $x=0.375$ and $1/3$ is shown in Fig. 2a and b, respectively. It can be seen from SEM micrographs clearly that the crystallinity of the synthesized powders is quite good and their crystal faces are well-developed. The particle size distribution (PSD) of the synthesized powders is more uniform than that of the powders synthesized by a solid-state process. It indicates that cathode powders with good crystallinity and uniform PSD can be synthesized by a sol–gel process. Decreasing the Co content or increasing the Mn content leads to decrease the particle size of the synthesized materials. It is consistent with our previous report [3]. The average diameter of the particle size for the $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ powders was found to be an order of 0.3–0.4 μm which is slightly less than that of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder. The well-defined crystal faces and uniform particle size dis-

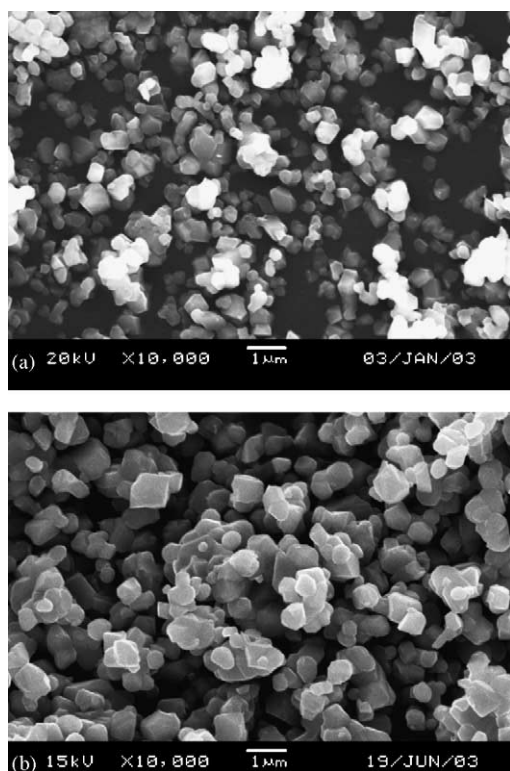


Fig. 2. Surface morphology for $x=0.375$ (a) and $x=1/3$ (b) in $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$.

tribution of the synthesized powders are expected to facilitate the fast lithium kinetics, resulting in high specific capacity and good cyclability [3,13].

The discharge capacity behavior of the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ ($1/3 \leq x \leq 1/2$) electrode at the first cycle is shown in Fig. 3. The discharge capacity of 192 and 188 mAh g^{-1} were obtained for $x=0.375$ and $1/3$, respectively. The initial specific capacity of $x=0.375$ is slightly higher than that of $x=1/3$. This is contributed from that the content of Ni with lower redox potential increases with an increase in the x value. The charge and discharge curves for the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ ($x=0.375$) electrode are shown in Fig. 4. It was found that the smooth charge and discharge curves of the electrode, suggesting that the electrode structure is stable and also provides a favorable network for faster lithium kinetics. The layered compounds exhibit

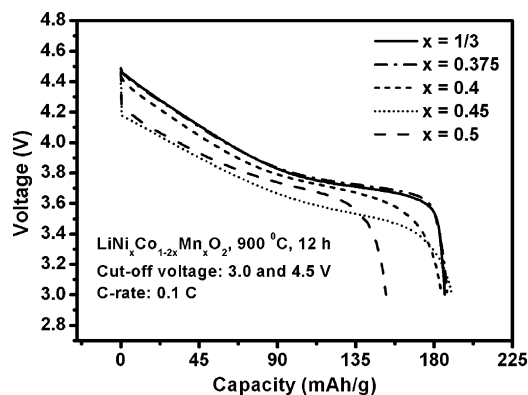


Fig. 3. Discharge curves for $x=1/3$, 0.375, 0.4, 0.45 and 0.5 in $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ at the first cycle.

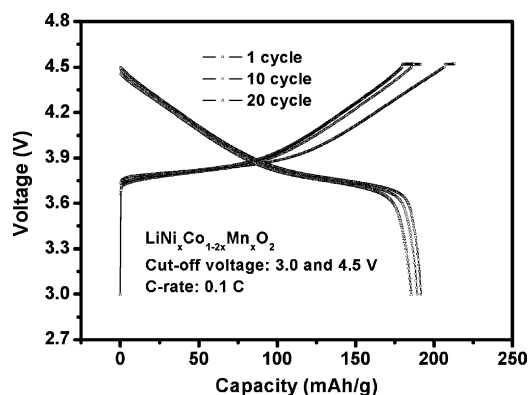


Fig. 4. Charge and discharge curves for $x=0.375$ in $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$.

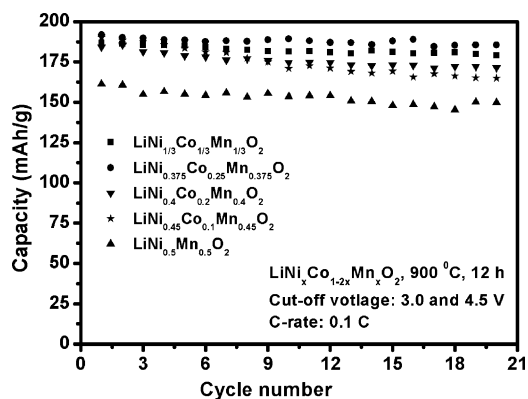


Fig. 5. Cyclability for $x=1/3$, 0.375, 0.4, 0.45 and 0.5 in $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$.

a double plateau at 4.0 V which suggests the occurrence of the phase transformation (layered to spinel structure) [14]. The absence of the double plateau at around 4.0 V confirms the structural stability of the synthesized powders is good during cycling. Fig. 5 shows the cyclability of the electrode at various x in the synthesized $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ powders. The discharge capacities of 188, 192, 185, 190 and 161 mAh g^{-1} , respectively, were obtained at the first cycle for $x=1/3$, 0.375, 0.4, 0.45 and 0.5. The specific capacity of $x=0.375$ is slightly higher than that of $x=1/3$. This is due to the increase of Ni and Mn contents in the electrode. After 20 cycles, the irreversible capacity of 1.5 mAh g^{-1} was obtained for $x=0.375$ and the capacity fading rate is 3.3%.

The electrochemical storage energy of the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ system was attributed to the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox reaction pair. This was confirmed from our previous in-reports on the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.1}\text{O}_2$ electrodes [5,15]. The oxidation states of Ni, Co and Mn were confirmed to be 2+, 3+ and 4+, in the pristine state and the oxidation states of Co and Mn remains the same at 3+ and 4+ during charge and discharge processes [5,15]. The substituted Co in the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ electrode can prevent its cation mixing between lithium layer and transition metal layer and stabilizes its structure resulting in better capacity retention and cyclability. In the present work, we have achieved the better structural and electrochemical properties of the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ system with increase of Ni and Mn contents by reducing the Co content. The structural parameters of the $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ powders are similar to those of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ compound. Meanwhile, the electrochemical performance of the $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ electrode, slightly better than that of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ compound, is the best among the synthesized materials. The $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ material with lower cost and better electrochemical properties than $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material are synthesized and characterized in this work.

4. Conclusion

The layered $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ ($1/3 \leq x \leq 1/2$) powders with good crystallinity and uniform particle size distribution were successfully prepared by a sol-gel process. The synthesized powders with single phase and layered structure were confirmed by the XRD analysis. The cation mixing slightly increases with a decrease in the Co content of the synthesized $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ powders. No undesirable cation mixing is observed in the $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders. The best cyclability and highest initial specific capacity (192 mAh g^{-1}) were obtained for $x=0.375$ in the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ system at 0.1 C rate in the potential range of 3.0–4.5 V. The structural parameters of the $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ powder are similar to those of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ one but the electrochemical performance of the $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$ electrode is slightly better than that of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode. Thus, the increase of low cost Ni and Mn in the $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ system can reduce its production cost.

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