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Influences of transition metal on structural and electrochemical properties of $Li[Ni_xCo_yMn_z]O_2$ (0.6 $\leq x \leq 0.8$) cathode materials for lithium-ion batteries

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Abstract: $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ (0.6 \leq x \leq 0.8) cathode materials with a typical hexagonal α -NaFeO₂ structure were prepared utilizing a co-precipitation method. It is found that the ratio of peak intensities of (003) to (104) observed from X-ray diffraction (XRD) increases with decreasing the Ni content or increasing the Co content. The scanning electron microscopy (SEM) images reveal that the small primary particles are agglomerated to form the secondary ones. As the Mn content increases, the primary and secondary particles become larger and the resulted particle size for the Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2 is uniformly distributed in the range of 100–300 nm. Although the initial discharge capacity of the Li/Li[Ni_xCo_yMn_z]O_2 cells reduces with decreasing the Ni content, the cyclic performance and rate capability are improved with higher Mn or Co content. The Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2 can deliver excellent cyclability with a capacity retention of 97.1% after 50 cycles.

Key words: Li[Ni_xCo_vMn_z]O₂; electrochemical performance; cathode material; lithium-ion battery

1 Introduction

Lithium-ion batteries (LIBs) possess numerous outstanding features including high energy density, excellent conversion efficiency, improved safety and long cycle life [1,2]. It is important to research the promotion of cathode materials in the application potential of LIBs. Note that layered LiCoO₂ has been limited by the relatively low specific capacity and high cost of cobalt [3], and olivine LiFePO₄ and spinel LiMn₂O₄ also do not exhibit high enough gravimetric and volumetric energy densities [4-6]. In comparison, lithium nickel cobalt manganese oxides have been investigated as advanced positive electrode materials for lithium-ion batteries, in which Ni-rich material Li[Ni_xCo_vMn_z]O₂ (NCM) ($x \ge 0.6$) [7–9] has attracted significant interest as a promising cathode material for application in plug-in hybrid vehicles (PHEVs) and electric vehicles (EVs), mainly coming from its high capacity of LiNiO₂, good cycle performances and excellent rate capability of LiCoO₂, and low price and safety of LiMnO₂ [10-16].

Since OHZUKU and MAKIMURA [17] first proposed that Li[Ni1/3Co1/3Mn1/3]O2 material owned excellent cyclability in 2001, many researchers [18-21] have extensively focused on the Li[Ni_xCo_vMn_z]O₂ material with various as-tuned values of x, y and z. Even though Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂ has shown poor cycle life and safety issues, it can provide high capacity of approximately 200 mA h/g, still remaining attractive for high-energy batteries [22]. In consideration of maintaining its high capacity, it is indispensable for substitutions of Ni with Co and/or Mn to stabilize its structural stability and further improve its electrochemical performances. Conversely, Ni is beneficial to increasing the lattice cell and the specific capacity, but the over-high content of Ni can lead to more cation mixing and exhibits irreversible initial capacities [23,24]. Though Co incorporation is effective to suppress the migration of transition metal ions into the Li sites, the increase of Co content can result in a decrease of the lattice cell and a reduction in specific capacity [25,26]. It should be noted that Mn is

Foundation item: Project (21473258) supported by the National Natural Science Foundation of China; Project (13JJ1004) supported by the Distinguished Young Scientists of Hunan Province, China; Project (NCET-11-0513) supported by the New Century Excellent Talents in University, China electrochemically inactive to maintain the structural stability of the α -NaFeO₂ phase, while superfluous Mn might suffer from a phase transition from a layered structure to a spinel one [27–29].

So far, the optimum compositions of transition metal ions in Li[Ni_xCo_yMn_z]O₂ ($x \ge 0.6$) for high capacity and acceptable thermal stability have not been clearly understood. Additionally, the core-shell-structured and concentration-gradient cathode materials based on lithium nickel cobalt manganese oxides [30–32], showing outstanding cycling performances and thermal stability as well as high reversible capacity, have been considered as urgent areas of research focus. Hence, it is necessary to systematically study the Li[Ni_xCo_yMn_z]O₂ ($x \ge 0.6$) in efforts to produce desirable cathode materials. To our knowledge, there are few studies reported for interchangeable Co and Mn replacement for Ni in type of Li[Ni_xCo_yMn_z]O₂ ($x \ge 0.6$) cathode materials.

In this work, the effects of the transition metal composition on the structural and electrochemical properties of Li[Ni_xCo_vMn_z]O₂ ($0.6 \le x \le 0.8$) applied in LIBs were reported, and the variation of Co and Mn interchangeable substitution Ni for in Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂ was investigated in details. The optimal composition of the lithium transition metal oxide $Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ with uniform size, excellent cycle performance and rate capability was obtained, which established the foundation for full concentration gradient cathode materials in Li[Ni_xCo_yMn_z]O₂ ($0.6 \le x \le 0.8$). We will use the following abbreviations, for x=0.8, y=0.1, z=0.1, 811; x=0.7, y=0.2, z=0.1, 721; x=0.7, y=0.1, z=0.2, 712; x=0.6, y=0.2, z=0.2, 622, respectively.

2 Experimental

 $Li[Ni_xCo_vMn_z]O_2$ (811, 721, 712, 622) powders with different kinds of metal compositions were prepared by the co-precipitation method followed by solid-state reaction. The appropriate amounts of NiSO₄·6H₂O, CoSO₄·7H₂O, and MnSO₄·5H₂O were undertaken as the starting materials and dissolved in the distilled water. The transition metal sulfate solution with a concentration of 2.0 mol/L was slowly dripped into the beaker (150 mL) under a N₂ atmosphere. Concurrently, a 2.0 mol/L NaOH solution (aqueous) as a coprecipitating agent was used to adjust the pH value and the desired amount of NH₄OH solution (aqueous) as a chelating agent was separately pumped into the continuously stirred beaker at a constant rate. The reactor temperature was maintained at 60 °C for 4 h with closely controlling the concentration, pH value, temperature, and stirring speed of the mixture. The obtained precipitate was filtered and washed several times to ensure that the residual ions (Na⁺, SO₄²⁻, or others) were almost removed. The precipitate was then dried in a vacuum

oven at 40 °C for 12 h to remove the adsorbed water, and the $[Ni_xCo_yMn_z](OH)_2$ (811, 721, 712, 622) precursor with a homogeneous distribution was obtained. LiOH and $[Ni_xCo_yMn_z](OH)_2$ (811, 721, 712, 622) with the molar ratio of 1.02 were thoroughly mixed in ethanol using a mortar and pestle, which were preheated to 480 °C for 4 h with the heating rate of 4 °C/min in the flowing oxygen atmosphere, and then calcined for 15 h at various temperatures [18,19,31,33,34]: 780 °C for 811, 800 °C for 721, 820 °C for 712 and 850 °C for 622. The main reason is that the materials 811, 721,712 and 622, which have different Ni contents, need different calcine temperatures.

Powder X-ray diffraction (XRD, Rigaku, Rint–2000) using Cu K_a radiation was employed to identify the crystalline phases of the prepared powders at each stage. The XRD data were obtained in the 2θ range of 10° – 80° in a continuous scan mode with a step size of 0.02° . The lattice parameters of Li[Ni_xCo_yMn_z]O₂ (811, 721, 712, 622) were calculated from the XRD patterns using the least-squares method based on the space group *R3m*. The morphologies of the prepared powders were observed using scanning electron microscopy (SEM, JSM–6510, JEOL, Japan). Chemical compositions (lithium and metals) of the obtained powders were determined by atomic absorption analysis (Vario 6, Analyticjena, Germany) and are summarized in Table 1.

The cell consisted of a positive cathode and a lithium metal anode separated by a porous polypropylene film. Positive electrodes were fabricated using a mixture of Li[Ni_xCo_vMn_z]O₂ active materials (80%), carbon black (10%), and polyvinylidene fluoride (10%) (mass fraction) in N-methyl-pyrrolidone. The slurry was cast onto aluminum foil and dried at 110 °C for 12 h in a vacuum oven. The electrochemical characterizations were tested using 2016 coin-type cells equipped with a Li metal negative electrode and a counter electrode. The electrolyte solution was 1 mol/L LiPF₆ in a mixture of ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate (volume ratio of 1:1:1, PANAX ETEC Co. Ltd., Korea). The cells were assembled in an argon filled glove box (MB-Labstar (1200/780), M.Braun Inertgas-Systeme GmbH, Germany) where both the moisture and oxygen contents were less than 1×10^{-6} . Cycling tests were performed at a 0.2C rate (0.1C=20 mA/g) in the voltage range of 2.8-4.3 V (vs Li⁺/Li) at room temperature using a BT2000 Battery testing system (BT2000-10V10A8CH, ARBIN Corporation, USA).

3 Results and discussion

The results of chemical analysis for $\text{LiNi}_x \text{Co}_y \text{Mn}_z \text{O}_2$ (811, 721, 712, 622) are shown in Table 1, confirming that the samples prepared by the mixture of hydroxide method possess a composition similar to the nominal

ratio in the mixtures.

Table 1 Chemical compositions of as-prepared samples $Li[Ni_xCo_yMn_z]O_2$ (811, 721, 712, 622)

811	721		
$Li_{1.00}[Ni_{0.79}Co_{0.11}Mn_{0.09}]O_2$	$Li_{1.01}[Ni_{0.70}Co_{0.21}Mn_{0.10}]O_2$		
712	622		
$Li_{1,02}[Ni_{0,71}Co_{0,11}Mn_{0,10}]O_{2}$	$I_{i_0} = [N_{i_0} = C_{i_0} = M_{i_0} = C_{i_0}$		

Figure 1 shows the XRD patterns of cathode material LiNi_xCo_vMn_zO₂ (811, 721, 712, 622) powders. A layer structure based on a hexagonal α -NaFeO₂ structure (space group: R3m) is observed for all of the powders without any obvious impurities and secondary phases. Note that for x=0.8 in 811 (Fig. 1(a)), the split peaks of (006)/(102) and (108)/(110) are hard to distinguish from each other, which become better defined by decreasing the amount of Ni in Figs. 1(b)-(d), suggesting more developed crystalline layer materials. It means that higher Ni content can bring less-ordered layer structure from split peaks. In fact, these are also evidenced from the ratio of relative intensity of (003) and (104) peaks. It is well known that the intensity ratio of $I_{(003)}/I_{(104)}$ is utilized as the major indication of cation mixing [29], where a small amount of nickel ions ($r_{Ni}^{2+}=0.69$ Å) may take place of lithium ions (r_{Li} +=0.76 Å) in the Li layer. It is shown that the Ni²⁺ in the Li layer cannot only decrease the discharge capacity but also slow down the diffusivity of Li⁺, while such structural disorder is



Fig. 1 XRD patterns of as-prepared $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$: (a) 811; (b) 712; (c) 721; (d) 622

considered as a main cause for this kind of poor electrochemical performance [23,24].

Table 2 shows the structural parameters of LiNi_xCo_yMn_zO₂ (811, 721, 712, 622) and the intensity ratio of the $I_{(003)}/I_{(104)}$. The intensity ratio of the $I_{(003)}/I_{(104)}$ increases from 1.085 in 811 to 1.336 in 622 as the Ni content decreases, which is clearly resulted from the similar ionic radius of Ni²⁺ and Li⁺.

However, the intensity ratio of 721 exceeds that of 712, which may come from the increase of the content of Co, since higher ratio of $I_{(003)}/I_{(104)}$ can be found for LiCoO₂ which shows clear split peaks of (006)/(102) and (108)/(110) pairs as well [19,27]. In consideration of the ionic radius of Ni²⁺ (0.69 Å), Ni³⁺ (0.60 Å), Co³⁺ (0.54 Å), and Mn^{4+} (0.53 Å), with the decrease of Ni content in LiNi_xCo_vMn_zO₂ (811, 721, 712, 622), the values of lattice parameter of c and unit cell volume increase, which can be attributed to the Mn or/and Co substitution for Ni, leading to the increased Ni²⁺ concentration from partial reduction of Ni³⁺ caused by balancing the cation and anion in LiNi_rCo_vMn_zO₂ (811, 721, 712, 622) [27]. In addition, no apparent trend in the lattice parameter of a is found as the Mn content decreases. As discussed above, it should be noted that the change of the Mn content is not a simple substitution reaction, and it is believed that its structure can also be influenced by other transition metal ions and sintering temperature [29].

Figures 2(a)–(d) illustrate the SEM images of these four as-prepared $[Ni_xCo_yMn_z](OH)_2$ (811, 721, 712, 622) powders, respectively. The morphologies of the samples show large agglomerates composed of rather small layered particles with the size in the range of 100–300 nm. The formation of the hydroxide precipitate can be attributed to the primary chemical precipitation from cations and hydroxyl groups, which grew and agglomerated in the violent stirring solution.

As the Mn content increases and the Ni content decreases, the shape of primary and secondary particles changes from a thin thread type to a thick one and exhibits uniform particle size distribution. Therefore, it is proposed that the Mn content has much influence on the morphological characteristics of the $[Ni_xCo_yMn_z](OH)_2$ particles [27,35].

Figure 3 shows the morphologies of primary particles on the surfaces of he $Li[Ni_xCo_yMn_z]O_2$

Table 2 Structural parameters and intensity ratio of $I_{(003)}/I_{(104)}$ of Li[Ni_xCo_yMn_z]O₂ (811, 721, 712, 622)

 $\frac{1}{(003)} = \frac{1}{(003)} = $								
$Li[Ni_xCo_yMn_z]O_2$	a/Å	$c/\text{\AA}$	<i>c/a</i> ratio	Unit cell volume/Å ³	$I_{(003)}/I_{(104)}$ ratio			
$Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$	2.8763(8)	14.1895(4)	4.933	101.67(1)	1.085			
$Li[Ni_{0.7}Co_{0.2}Mn_{0.1}]O_2$	2.8731(6)	14.2032(7)	4.943	101.93(5)	1.231			
$Li[Ni_{0.7}Co_{0.1}Mn_{0.2}]O_2$	2.8739(6)	14.2162(4)	4.946	102.33(3)	1.205			
$Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$	2.8715(0)	14.2184(7)	4.951	102.53(7)	1.336			

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Fig. 2 SEM images of as-coprecipitated [Ni_xCo_yMn_z](OH)₂ hydroxides: (a) 811; (b) 721; (c) 712; (d) 622



Fig. 3 SEM images of $Li[Ni_xCo_yMn_z]O_2$: (a) 811; (b) 721; (c) 712; (d) 622

(811, 721, 712, 622) powders calcined at different temperatures. It is clear that smoothly edged polyhedron and round particles are observed instead of layered ones on the surface of hydroxides after the heat treatment.

Irregular shape and serious aggregation can be found for 811 powders, as shown in Fig. 3(a), while 622 powders exhibit relative large primary particles with narrow size distribution, suggesting that the compounds with higher Mn and Co contents cannot only tune the morphology and distribution but also improve their electrochemical properties [19,35,36].

Figure 4 illustrates the initial voltage versus capacity curves on charge and discharge between 2.8 and 4.3 V for cells with Li metal anodes and cathodes of the following materials: Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂ (811), Li[Ni_{0.7}Co_{0.2}Mn_{0.1}]O₂(721), Li[Ni_{0.7}Co_{0.1}Mn_{0.2}]O₂ (712), and Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O₂ (622) at a constant current density of 20 mA/g (0.1C). The initial discharge capacity of Li/Li[Ni_xCo_yMn_z]O₂ cells reduces with decreasing the Ni content with the values of 202.2 mA·h/g for 811, 186.8 mA·h/g for 721, 182.0 mA·h/g for 712 and 173.4 mA h/g for 622, which indicates that Ni is a main redox species in the host structure during the tested range.



Fig. 4 Initial charge–discharge capacities of Li/Li[Ni_xCo_yMn_z]O₂ cells at current density of 20 mA/g between 2.8 and 4.3 V at 25 °C

It is also found that the irreversible capacities of $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ (811, 721, 712, 622) vary considerably with the formation of the solid electrolyte interphase (SEI) layer and the loss of lithium [37,38]. Meanwhile, the initial discharge capacity of 721 is greater than that of 712, showing that the increased Co content in the $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ can reduce the resistance of the diffusion of lithium ions [36].

Figure 5 shows the discharge capacity versus the cycle number of the Li/ Li[Ni_xCo_yMn_z]O₂ (811, 721, 712, 622) cells between 2.8 and 4.3 V at a constant current density of 40 mA/g (0.2*C*). As is well known, Ni-rich

Li[Ni_xCo_yMn_z]O₂ ($x \ge 0.6$) typically suffers from poor Li⁺ intercalation stability, which results from the formation of a more stable spinel phase or stable Li_xNi_{1-x}O phase [29,39,40], leading to an increase of the interfacial resistance upon cycling.



Fig. 5 Discharge capacity vs number of cycles of Li/Li[Ni_xCo_yMn_z]O₂ cells in voltage range of 2.8–4.3 V at 25 °C

Although the Li/Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂ cell deliveres the highest initial discharge capacity of 197.7 mA h/g, it shows gradual capacity fade during cycling and reaches 87.8% capacity retention after 50 cycles, which can be primarily ascribed to the structural transformation near the surface region that increases the charge-transfer resistance between the positive electrode and the electrolyte upon electrochemical cycling [27,41]. Meanwhile, though the Li/Li[Ni_xCo_yMn_z]O₂ (721, 712, 622) cells with decreased Ni content have lower initial capacities, they show much better capacity retention over the same cycling period, voltage range and temperature: 95.1% for 721, 91.7% for 712, and 97.1% for 622 after 50 cycles. It is believed that the enhanced capacity retention may be partly attributed to the enhanced structural stability coming from the decrease of cation mixing and the increase of stable tetravalent Mn ions [27,42].

The rate capabilities of the Li/Li[Ni_xCo_yMn_z]O₂ (811, 721, 712, 622) cells are shown in Fig. 6. Each cell was firstly charged galvanostatically at 0.1*C* (20 mA/g) until the voltage reached 4.3 V and then discharged at 0.2*C* (40 mA/g), 0.5*C* (100 mA/g), 1*C* (200 mA/g), 2*C* (400 mA/g), 5*C* (1000 mA/g) and 0.2*C* (40 mA/g) for every five cycles, respectively. As can be seen from Fig. 6, the rate capability of Li[Ni_xCo_yMn_z]O₂ is gradually improved with decreasing the Ni content, indicating that 721 and 622 may have slightly better rate performance, confidently that the rate capability can be improved with higher content of Co [36]. For example, the capacity of 811 at 5*C* is 70.4% of that at 0.2*C*, while

622 exhibits a much enhanced capacity retention of 82.2%. These results reveal that the enhanced rate capability with decreasing the Ni content can be mainly attributed to the decrease of cation mixing and polarization. It is equally important to consider the effects of the electronic conduction, lithium diffusion and charge transfer reaction (kinetics) on the performance of the materials [18,43].



Fig. 6 Comparison of rate capabilities of $\text{Li}/\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ cells at different rates between 2.8 and 4.3 V at 25 °C

4 Conclusions

1) Layer-structured Li[Ni_xCo_yMn_z]O₂ (811, 721, 712, 622) materials were obtained utilizing a co-precipitation method. The morphologies of the samples show that large agglomerates are composed of small and rock-shaped particles, and the material 622 exhibits uniform particle size distribution. The XRD patterns show that Li[Ni_xCo_yMn_z]O₂ (811, 721, 712, 622) with higher Ni content has less-ordered layer structure.

2) Though the initial discharge capacity of the Li/Li[Ni_xCo_yMn_z]O₂ (811, 721, 712, 622) cells reduces with decreasing the Ni content, the capacity retentions of 622, 721, 712 are superior to that of 811. Excellent cyclability is delivered for 622 with a capacity retention of 97.1% after 50 cycles.

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过渡金属对锂离子电池正极材料 Li[Ni_xCo_yMn_z]O₂ (0.6≤x≤ 0.8)结构和电化学性能的影响

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摘 要:利用共沉淀法制备具有典型六边形 α-NaFeO₂结构的正极材料 Li[Ni_xCo_yMn_z]O₂ (0.6≤x≤0.8)。XRD 结果表明:明: (003)峰与(104)峰的强度比随镍含量的减少而增加,随钴含量的增加而增加。SEM 结果表明:材料是由微小的初级颗粒聚集而成的二次颗粒,并且随锰含量的增加,初级颗粒和二次颗粒变大,同时 Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O₂颗粒分布比较均匀,颗粒大小为 100~300 nm。尽管锂离子电池 Li/Li[Ni_xCo_yMn_z]O₂ 的首次放电容量随镍含量的减少而减小,但是循环和倍率性能却随锰或钴含量的增加而得到改善。Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O₂ 具有良好的循环性能,在循环 50 次后还能保持 97.1%的容量保持率。

关键词:Li[Ni_xCo_yMn_z]O₂;电化学性能;正极材料;锂离子电池

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