

Synthesis and electrochemical characterization of layered $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ cathode material for Li-ion batteries^①

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Abstract: Layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials were synthesized using a nickel-cobalt-manganese carbonate precursor obtained by chemical coprecipitation. The $[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{CO}_3$ precursor and the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders were characterized by X-ray diffraction(XRD) and scanning electron micrograph(SEM). The SEM analysis shows that these particles possess uniform and spherical morphology. The electrochemical properties of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material for rechargeable lithium-ion batteries such as the galvanostatic charge-discharge performance and cyclic voltammetry(CV) were measured. The results show that an initial discharge capacity of $190.29 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ is obtained in the voltage range of 2.5–4.6 V and at a current rate of 0.1 C at 25 °C. The discharge capacity increases linearly with the increase of the upper cut-off voltage limit.

Key words: lithium-ion batteries; cathode material; layered structure; nickel-cobalt-manganese oxides

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1 INTRODUCTION

Due to the high cost of LiCoO_2 , a commonly used cathode material in commercial rechargeable lithium-ion batteries, much efforts have been made to develop cheaper cathode materials than LiCoO_2 . LiNiO_2 and LiMnO_2 have been studied extensively as possible alternatives to LiCoO_2 ^[1-4]. Stoichiometric LiNiO_2 is known to be difficult to synthesize and its multi-phase reaction during electrochemical cycling leads to structural degradation, and layered LiMnO_2 has a significant drawback in its crystallographic transformation to spinel structure during cycling^[5-7]. Recently, a concept of one-to-one solid solution of LiCoO_2 , LiNiO_2 and LiMnO_2 , i. e., $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, was adopted to overcome the disadvantage of LiNiO_2 and LiMnO_2 ^[8-12]. The layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is an attractive cathode material for rechargeable lithium-ion batteries in several aspects. In this research, layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was prepared using the nickel-cobalt-manganese carbonate precursor, and the electrochemical properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were investigated.

2 EXPERIMENTAL

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders were synthesized

by mixed carbonate method, an aqueous solution of metal nitrates was made with a cation ratio, $n(\text{Ni}) : n(\text{Co}) : n(\text{Mn}) = 1 : 1 : 1$, the precipitation of $[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{CO}_3$ was achieved by slowly dripping the nitrate solution to a NH_4HCO_3 solution with continuous stirring. The filtrated precipitate was washed with de-ionized water and dried in air, then mixed with stoichiometric amount of Li_2CO_3 by ball-milling. The mixed powders were heated at 480 °C for 6 h and then calcined at 950 °C for 16 h in air.

The thermal behavior of the precursor was examined by thermogravimetric analysis(TGA). The powder was characterized by X-ray powder diffraction measurements using a diffractometer PW 1710 with $\text{Cu K}\alpha$ radiation (Japan). The morphology of sample was observed using scanning electron microscopy (SEM, KYKY 2800, Japan). The electrochemical properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ as cathode materials were evaluated using prototype cell on LAND-2001A battery program-control test system, using a lithium metal foil as the anode and 1 mol/L LiPF_6 in a 1 : 1 solvent of Ethylene carbonate (EC) and Dimethyl carbonate (DMC) as electrolyte. The separator was made from a Celgard 2400 film microporous polypropylene membrane. The cells were assembled in argon gas filled glove-box.

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The microelectrode was produced in glove-box with the mixture of the samples and carbon black as the working electrode in ratio of 8:1 and with the pure-lithium foil as the count-electrode. The cyclic voltammetry curves were measured by Potentiostat/Gallanostat Model (Perkin-Elmer 273A, EG&E).

3 RESULTS AND DISCUSSION

The thermal behavior of the $[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{CO}_3$ precursor and Li_2CO_3 was examined by thermogravimetric analysis (TGA). From the TG and DTA results of the precursor, it reveals that below 350 °C, there is a mass loss due to the decomposition process of the carbonate compound. The mass loss of the specimens stops at temperatures above 480 °C until to 1080 °C (Fig. 1).

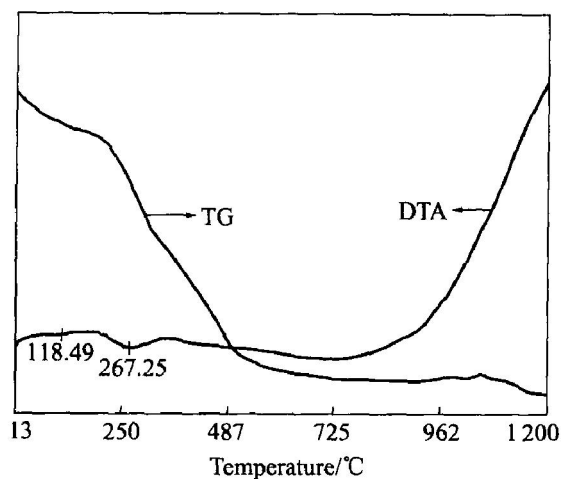


Fig. 1 TG and DTA curves of mixture of $[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{CO}_3$ precursor and Li_2CO_3

The XRD pattern of $[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{CO}_3$ precursor obtained by co-precipitation method is shown in Fig. 2(a). Although the XRD pattern of precursor has a low crystallinity, it is found that the precursor has a similar well-defined $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{CO}_3$ hexagonal structure ($a = 4.52 \text{ \AA}$, $c = 15.6 \text{ \AA}$) with no impurity phase. This would be attributed to the homogeneous powder precursor, in which Ni, Co and Mn are uniformly distributed in an atomic scale. The powder X-ray diffraction pattern of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ final sample is shown in Fig. 2(b). The XRD pattern is well defined and shows the hexagonal doublets (006)/(102) and (108)/(110) a clear splitting, which indicate that they have a high degree of crystallization, good hexagonal ordering and greater layered characteristics. The integrated intensity ratio of the (003) peak to (104) peak (R) in the XRD patterns is shown to be a measure of “cation mixing” and a value of $R < 1.2$ is an indication of undesirable cation mixing^[13, 14]. The ratio of the intensity

of the (003) peak to (104) peak of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ sample reported here was calculated to be $R = 1.42$, well above the values reported of undesirable cation mixing. The lattice parameters of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ are: $a = 2.866 \text{ \AA}$, $c = 14.262 \text{ \AA}$ and match with the values observed by Shaju et al^[4] and Yabuuchi et al^[15] ($a = 2.867 \text{ \AA}$ and $c = 14.246 \text{ \AA}$), and the c/a ratio is 4.976. The high value of c/a means that the de-intercalation/intercalation of Li^+ is more flexible.

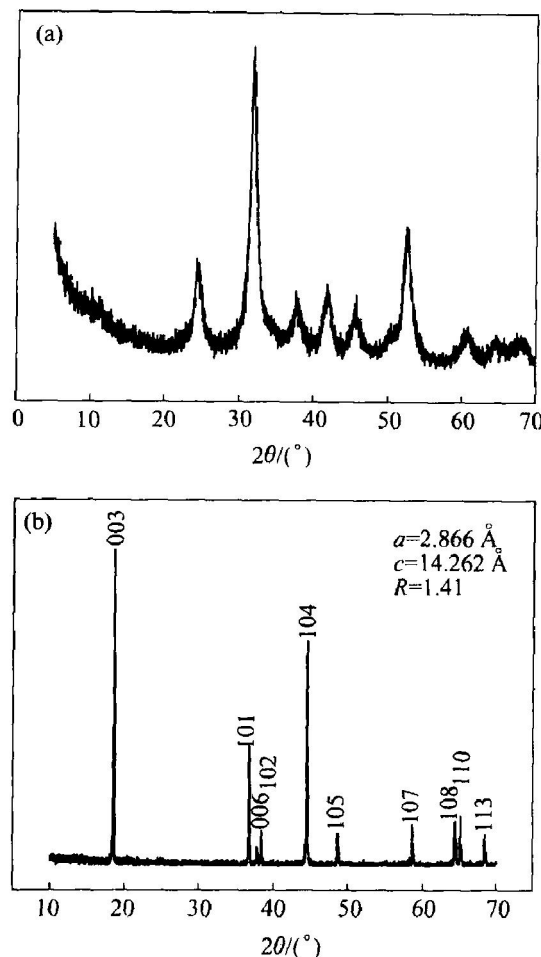


Fig. 2 XRD pattern of $[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{CO}_3$ precursor (a) and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ final sample (b)

The SEM images of precursor and final powders is shown in Fig. 3. It can be seen that particles in $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{CO}_3$ precursors and the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders possess spherical morphology. However, the size of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles is more uniform and in the range of 1–2 μm .

Fig. 4 shows the charge and discharge curves for the $\text{Li}/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell at a current rate of 0.1 C in voltage window 2.5–4.6 V at room temperature. As seen in Fig. 4, the initial discharged capacity of $190.29 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ is obtained. On starting the current, the voltage suddenly increases to about 4 V and then slowly decreases to 3.75 V and stays along an almost horizontal line at 3.75 V, until the charge capacity re-

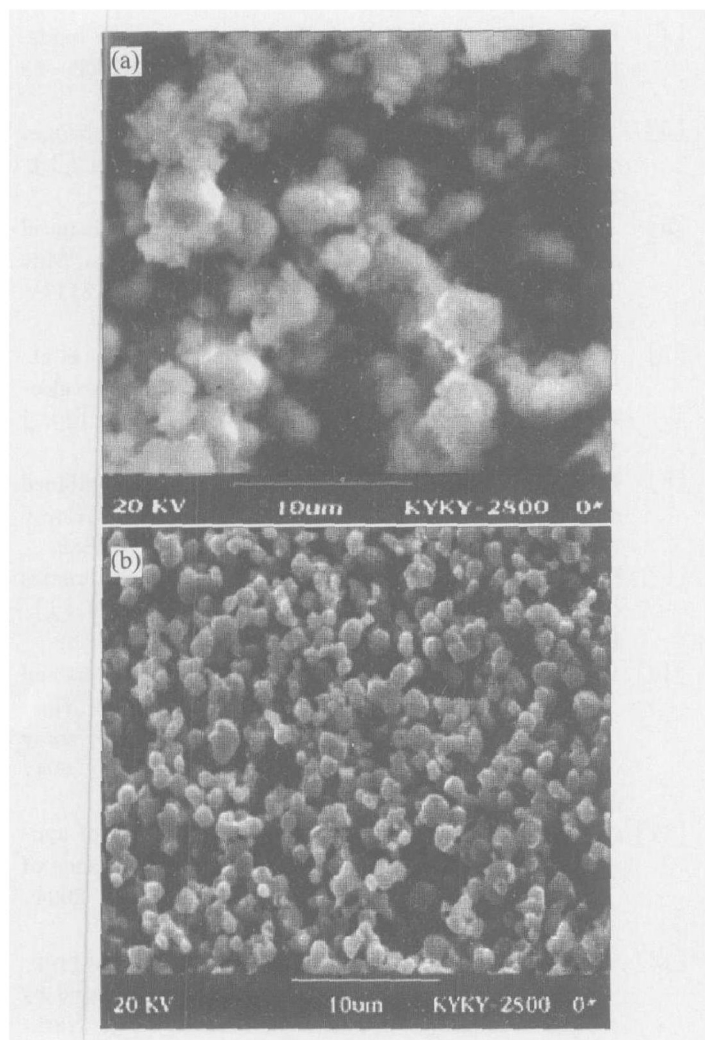


Fig. 3 SEM images of $[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{CO}_3$ precursor (a) and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ final sample (b)

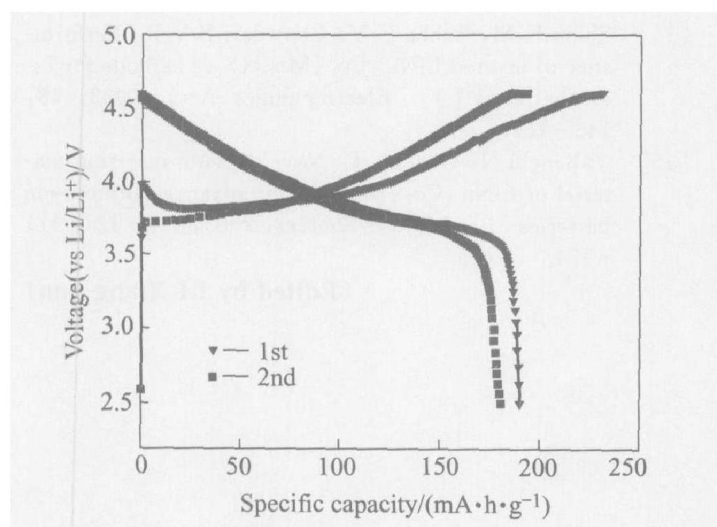


Fig. 4 Charge and discharge curves (at 0.1 C) of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder at 25 °C

ches about $95 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$. The slope in the voltage versus capacity curves increase at $95 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ and voltage curves linearly increase until voltage reaches 4.6 V, similar to that observed by Yabuuchi and Ohzuku^[15]. The irreversible capacity

observed in the first cycle is about $40 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$.

Fig. 5 shows the specific discharge capacity vs number of cycle for $\text{Li} / \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell at 25 °C at a constant current density of $0.1 \text{ mA} / \text{cm}^2$ in the different voltage range of 2.5–4.3, 2.5–4.4, 2.5–4.5 and 2.5–4.6 V. The specific discharge capacity increases linearly with the increase of the upper cut-off voltage limit, the discharge capacities of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode are 190.29, 172.25, 164.27 and 156.12 $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$, respectively, with good cycleability. The discharge capacities remain at 158.73, 153.59, 149.35 and 146.86 $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$ after 20 cycles, which are 83.42%, 89.17%, 90.92% and 94.07% of initial capacities, respectively.

Fig. 6 shows the cyclic voltammetry curve of the $\text{Li} / \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell between 2.8 V and 4.6 V at a scan rate of 0.05 mV/s at room

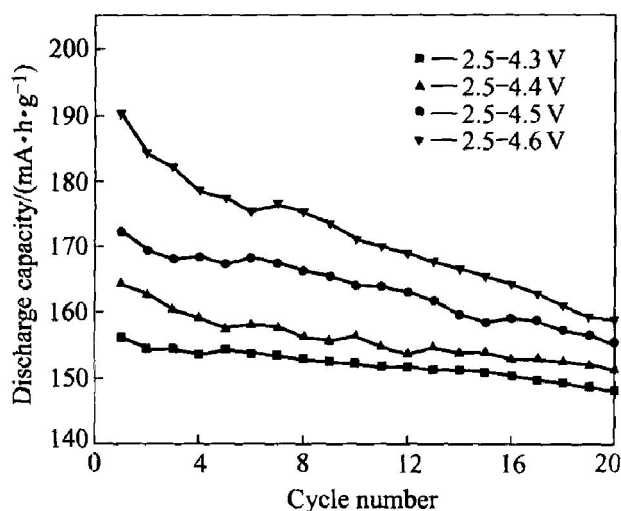


Fig. 5 Discharge capacity vs number of cycle for $\text{Li} / \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell at 0.1 C in different voltage range at 25 °C

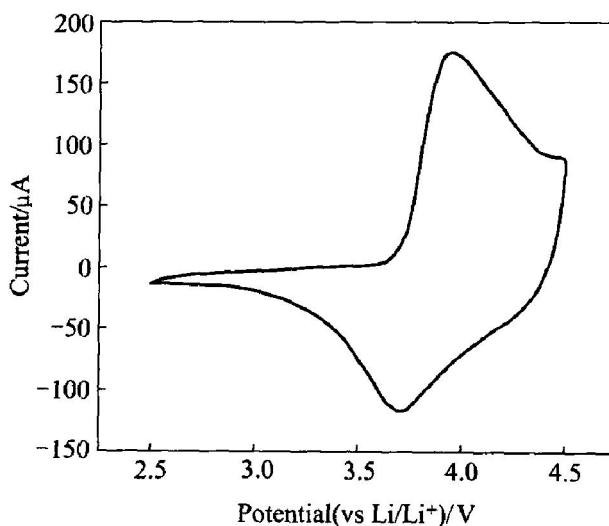


Fig. 6 Cyclic voltammetry curve of $\text{Li} / \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell between 2.5 V and 4.6 V at scan rate of 0.05 mV/s

temperature. As can be seen from Fig. 6, the main oxidation peak is observed at 3.9 V, while the reduction peak appears at 3.7 V, corresponding to $\text{Ni}^{2+}/\text{Ni}^{4+}$. The material has a couple of redox peak representing the de-intercalation of Li^+ from the initial structure that is observed in a narrow potential range. This implies that the extraction of Li^+ occurs easily from an ordered and stabilized layered structure of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

4 CONCLUSIONS

The layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was synthesized using a nickel-cobalt-manganese carbonate precursor and characterized by means of XRD, SEM, galvanostatic charge-discharge performance and cyclic voltammetry (CV). The lattice parameters obtained are: $a = 2.866 \text{ \AA}$ and $c = 14.262 \text{ \AA}$. The nicely split (006)/(102) and (108)/(110) peak in the XRD patterns reveal the layered structure of the compound. The initial discharge capacity of $190.29 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ was obtained in the range of 2.5–4.6 V and at a current rate of 0.1 C at 25 °C, and the discharge capacity increases linearly with the increase of the upper cut-off voltage limit. Cyclic voltammetry shows the major redox process at 3.7–3.9 V corresponding to $\text{Ni}^{2+}/\text{Ni}^{4+}$. The results indicate that the layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is an attractive cathode material for rechargeable lithium-ion batteries.

REFERENCES

- [1] Hung S T, Park H S, Choy J H. Evolution of local structure around manganese in layered LiMnO_2 upon chemical and electrochemical delithiation/relithiation [J]. *Chem Mater*, 2000, 12: 1818–1826.
- [2] Ceder G, Mishra S K. Stability of orthorhombic and monoclinic-layered LiMnO_2 [J]. *Electrochem Solid State Lett*, 1999, 2: 550–552.
- [3] Wang G X, Horvat J, Bradhurst D H, et al. Structural physical and electrochemical characterization of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ solid solutions [J]. *J Power Sources*, 2000, 85: 279–283.
- [4] Kelley T E, Mitchell P H. Lithium manganese oxide-based active material [P]. US 2002031667, 2002–03–14.
- [5] Li G H, Iijima Y, Kudo Y, et al. Structural changes of manganese spinel at elevated temperatures [J]. *Solid State Ionics*, 2002, 146: 55–63.
- [6] Aral H, Okada S, Sakurai Y, et al. Electrochemical and thermal behavior of $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Co}, \text{Mn}, \text{Ti}$) [J]. *J Electrochem Soc*, 1997, 144(9): 3117–3125.
- [7] Horn Y S, Hackney S A, Armstrong A R, et al. Structural characterization of layered LiMnO_2 electrodes by electron diffraction and lattice imaging [J]. *J Electrochem Soc*, 1999, 146: 2404–2412.
- [8] Hwang B J, Tsai Y W, Carlier D, et al. A combined computational experimental study on $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [J]. *Chem Mater*, 2003, 15: 3676–3682.
- [9] Kim J M, Chung H T. The first cycle characteristics of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ charged up to 4.7 V [J]. *Electrochimica Acta*, 2004, 49: 937–944.
- [10] Park S H, Yoon C S, Kang S G, et al. Synthesis and structural characterization of layered $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ cathode materials by ultrasonic spray pyrolysis method [J]. *Electrochimica Acta*, 2004, 49: 557–563.
- [11] Li D Ch, Muta T, Zhang L Q, et al. Effect of synthesis method on the electrochemical performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [J]. *J Power Sources*, 2004, 132: 150–155.
- [12] Wu Q, Cheng Y, Xu H, et al. Electrochemical properties of nano-sized $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ prepared by sol-gel method [A]. IMLB 12 Meeting [C]. Nara, Japan: The Electrochemical Society, Inc, 2004.
- [13] Koyama Y, Tanaka I, Adachi H, et al. Crystal and electronic structures of superstructural $\text{Li}_{1-x}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ [J]. *J Power Sources*, 2003, 119–121: 644–648.
- [14] Shaju K M, Subba G V, Chowdari B V R. Performance of layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ as cathode for Li ion batteries [J]. *Electrochimica Acta*, 2002, 48: 145–151.
- [15] Yabuuchi N, Ohzuku T. Novel lithium insertion material of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ for advanced lithium-ion batteries [J]. *J Power Sources*, 2003, 119–121: 171–174.

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