

A Spray-drying Method to Synthesis $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and Its Electrochemical Characteristics as a Cathode Material*

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Abstract : Spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ materials were prepared via a spray-drying method. The materials were sub-micro size particles , and the particles had a well-defined cubic spinel structure. For Li-ion batteries , the electrochemical property of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ were characterized by cycling the cells between 3.20 V and 4.95 V at a specific current density. The spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ delivered an initial discharge capacity of 132 mAh/g and exhibited good cycle stability at room temperature. Cycling at high voltage range (4.50 ~ 4.95 V) and low voltage range (3.20 ~ 4.50 V) , the discharge capacities of materials were about 100 mAh/g and 25 mAh/g respectively , and both exhibited good cycle ability. However , at high temperature , the materials showed different electrochemical characteristics.

Key words : $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$; spray-drying method ; electrochemical characteristics ; lithium ion batteries

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Recently , transition metal-substituted spinel materials ($\text{LiMn}_{2-x}\text{M}_x\text{O}_4$, $\text{M} = \text{Cr} , \text{Co} , \text{Fe} , \text{Ni} , \text{Cu}$) have drawn a lot of attention due to its high voltage plateau at around 5 V and high specific energy^[1-4]. The capacity and voltage plateau in Li/ $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ cells strongly depend on the type of transition metals (M) and their content. Among those materials , $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ has been concerned especially of its high discharge capacity and dominant plateau around 4.7 V. $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ shows good cycle stability on repeated Li ion extraction and insertion , making it the most attractive material for practical use^[2,5]. In general , $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ was prepared by a conventional solid - state method^[6,7]. However , it requires prolonged heat treatment at relatively high temperatures with repeatedly intermediate grinding. Moreover , this method does not provide good control on the crystalline growth , compositional homogeneity , morphology and microstructure. The wet method , like as sol-gel method^[4,8] , which can produce highly homogeneous sub-micron sized particles with a narrow particle size distribution , has been developed. But the sol-gel method has a complex synthesis route and high synthetic cost.

Now , a spray-drying method has been introduced to synthesise ultra - fine LiCoO_2 , sub-sized LiMn_2O_4 and spherical $\text{Li}_{1+x}\text{V}_3\text{O}_8$ successfully^[9-11]. In this present work , the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ has also been prepared by this method , which can solve the disadvantages of the solid - state method and sol-gel method. The structure , morphology and electrochemical properties of the products have

been investigated.

1 Experimental

Stoichiometric amounts of $\text{CH}_3\text{COOLi} \cdot 4\text{H}_2\text{O}$, Mn (CH_3COO)₂ · 4H₂O , Ni (CH_3COO)₂ · 4H₂O were dissolved in distilled water. The result solution was dried to form a mixed dry precursor via a spray-dryer. The solution was atomized via a sprinkler at an air pressure of 0.2 MPa , and was dried in the spray-dryer by hot air. The inlet air temperature was 220 °C , and the exit air temperature was 110 °C. The as-prepared powders were annealed at 400 °C under an air atmosphere for 4 h. Then the obtained products were ground in an agate mortar and re-annealed at 800 °C for 24 h. Powder X-ray diffraction (XRD Rigaku D/max-rA) using Cu K_α radiation was used to identify the crystalline phase of the powders. The particle morphology , and size were observed using a field-emission scanning electron microscopy (FSEM SIRION JY/T010-1996).

A slurry consisting of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powder as active material , conducting agent (acetylene black) , and binder (polyvinylidene fluoride) was pasted onto an aluminum foil , with NMP (*n*-methylpyrrolidone) as the solvent. The weight ratio of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ active powder , conducting agent and binder was 70 : 15 : 15 in the working electrode. After drying in air at 80 °C for 4 h , the sheet was pressed under pressure of 20 MPa to provide increased adherence of the cathode mixture onto the aluminum foil current collector. The weight of active materials

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in the electrode sheet was about 4.01 mg of in a square centimeter of aluminum foil. After drying in vacuum at 120 °C for 24 h , the electrodes were assembled into the cells in an Ar-filled glove box. The metallic lithium sheet was used as the counter electrode. A solution of 50 % ethylene carbonate (EC), 50 % dimethyl carbonate (DMC) and 1 mol/L LiPF_6 was used as electrolyte solution and a polypropylene (PP) film Cellgard 2300 as separator. The electrochemical properties of the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ electrodes were measured by cycling the cells between 3.20V and 4.95V with a specific current density (a nominal specific capacity of 140 mAh/g was assumed to convert the current density into C rate).

2 Results and discussion

Fig.1 shows XRD pattern of as-synthesized $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders. The $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders were found to have a well - defined spinel structure , besides a small NiO peaks as an impurity appeared. This result is in agreement with the previous literature^[1] , which shows when annealed above 600 °C , low-crystalline , pure spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders decomposed into mixture of spinel phase and a small mount of NiO . A SEM image of the spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders is shown in Fig.2. The particle size was less than 1 μm and exhibited uniform particle size distribution .

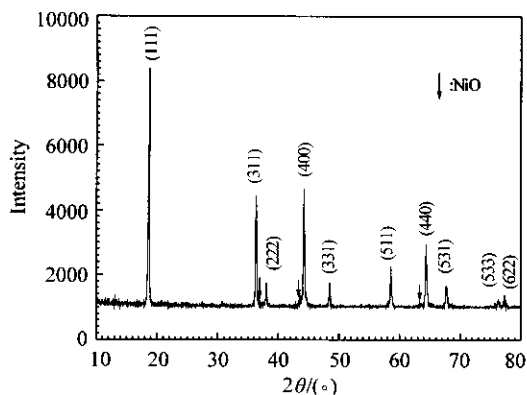


Fig.1 X-ray diffraction patterns of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders

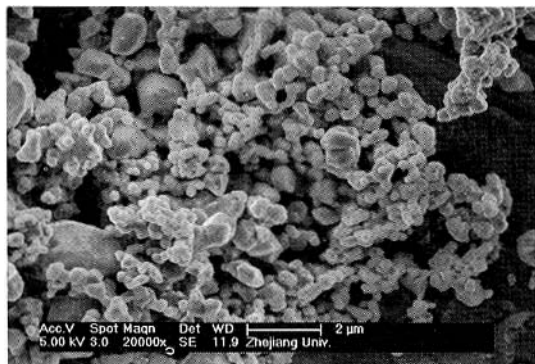


Fig.2 SEM images of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders

Initial charge/discharge curves for the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ electrode between 3.20 ~ 4.95 V at a current density of 112.0 $\mu\text{A}/\text{cm}^2$ (1/5 C rate) is presented in Fig.3. The upper voltage was limited to 4.95 V for fear of possible electrolyte decomposition , especially upon extended cycling. The curves show a multiple number of distinct plateaus at different voltage regions , a small 4 V plateau and a concrete 4.7 V plateau in the initial charge /discharge process and next. This indicates that the electrodes undergo multiple stages of reversible oxidation and reduction processes. In Fig.4 , the cyclic voltammetric profile of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ showed three reversible couples , which were related to the various phase transitions between the reaction stages. In high voltage , the large peaks are the redox couple Ni^{2+} to Ni^{4+} , which resulted in the long charge/discharge plateau around 4.7 V in Fig.3. The 4 V plateau is oxidation of Mn^{3+} to Mn^{4+} ^[12] , and so , the corresponding small peaks are shown around 4 V in Fig.4. The electrode delivers a discharge capacity of 132 mAh/g in total during the initial cycle , and the initial charge capacity is 143 mAh/g. From the Fig.3 , most discharge capacity (about 80% in total) presents in the plateau of 4.7 V .

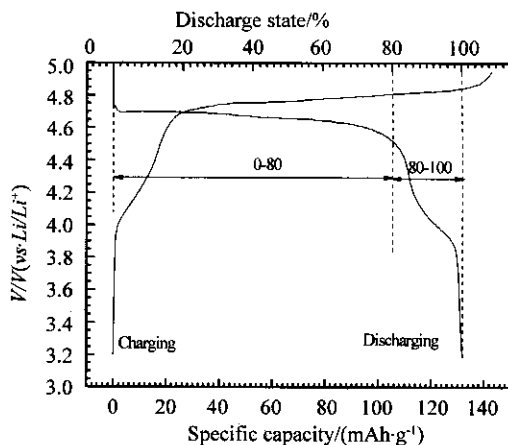


Fig.3 Initial charge/discharge curves at a current density of 112.0 $\mu\text{A}/\text{cm}^2$ (1/5 C rate) in voltage range 3.20 ~ 4.95 V for $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders

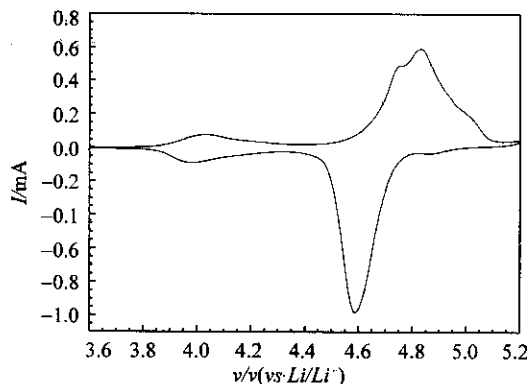


Fig.4 Cyclic voltammograms for $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cells at 0.05 mV/s scan rate

For comparison, at room and high temperatures, the cycling performance of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ were studied at different charge/discharge voltage range with the respective 1C rate current density, as shown in Fig.5. $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ showed a stable cycling behavior at room temperature, and after 50 cycles the discharge capacity was over 110 mAh/g. However, at high temperature, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ presented a very poor cycling performance with only cycle retention rate of 20% after 50 cycles. From Fig.5 (c) and Fig.5 (d), $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ exhibited different cycling property at different cut-off voltage at room temperature. At 3.20 ~ 4.50 V, the discharge capacity was only about 25 mAh/g, but after 50 cycles, there were not any capacities faded. These are due to the transition metals (Ni) substituted part of Mn, which may stabilize the spinel structure of the host compound, although often at the cost of lower 4-V capacity, but solve the Jahn-Teller distortion. So in the 4-V region, the products showed an excellent cycling performance and a lower 4-V capacity. From Fig.3, the capacity was present in the voltage range of 4.50 ~ 4.95 V. In this high range, the initial discharge capacity was about 100 mAh/g, and the cycle performance was not as good as the 4-V region, however, after 50 cycles, the capacity still maintained above 80 mAh/g. Based on these results, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ may be used as high-voltage materials.

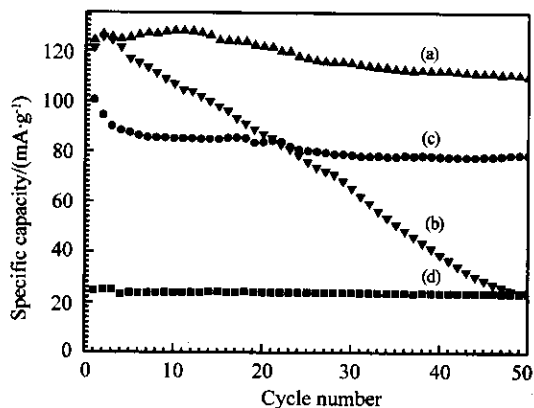


Fig.5 Cycling performance of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders :
(a) 25°C at 3.20 ~ 4.95V ; (b) 50°C at 3.20 ~ 4.95V ;
(c) 25°C at 4.50 ~ 4.95V ; (d) 25°C at 3.20 ~ 4.50V

3 Conclusions

Spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powders were prepared by a spray-drying method and studied as high-voltage cathode materials. The materials were obtained by re-annealing the powders after annealing the precursor in air. The sub-micro size products had a cubic spinel structure, and two plateaus in the charge/discharge curves above 4 V. At room temperature, the material delivered a capacity of 132

mAh/g on the first cycle and sustained a value of 110 mAh/g even after 50 cycles at the charge/discharge voltage range of 3.20 ~ 4.95V. In this charge/discharge process, a majority of capacity (about 80% in total) was discharged at high-voltage region. At high temperature, the materials exhibited a poor cycle performance.

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喷雾干燥法制备 $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ 及其电化学性能

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摘要：采用喷雾干燥方法合成了高电压锂离子电池正极材料 $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ，并研究了其电化学性能。研究发现，室温条件下，在 3.20 ~ 4.95 V 的充放电电压范围， $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ 的首次可逆容量为 132 mAh/g，并显示出良好的循环性能，在 3.20 ~ 4.50 V 和 4.50 ~ 4.95 V 两个电压区间内，首次可逆容量分别为 25 和 100 mAh/g。而在高温下，该电极材料的电化学性能发生了明显的改变。

关键词： $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ；喷雾干燥法；锂离子电池；电化学性能

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