

ORIGINAL RESEARCH ARTICLE

Preparation and Study of Waterborne Asphalt Pavement Maintenance Agent

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ABSTRACT

The precursor $\text{Ni}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ was prepared by coprecipitation method. The precursor was mixed with $\text{Mg}(\text{OH})_2$ / $\text{Zn}(\text{NO}_3)_2$ / TiO_2 and $\text{LiOH}\cdot\text{H}_2\text{O}$, Li_2CO_3 to synthesize doped lithium ion layer positive electrode material $\text{Li}[\text{Ni}_{0.8-x}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Mx}]_2\text{O}_2$ ($x = 0.04$). The effects of synthesis conditions on the chemical properties of the composites were discussed. The synthesized samples were prepared by scanning electron microscopy (SEM), thermogravimetry - differential thermal analysis (TG / DTA), X - ray diffraction (XRD) and constant current charge - Testing and characterization. The results show that the crystallinity of $\text{Li}[\text{Ni}_{0.8-x}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Mx}]_2\text{O}_2$ ($x = 0.04$) prepared at 900°C for 20 h is good, and it has good layered structure. The properties of the doped elements The results show that the electrochemical performance of the samples with Mg and Zn is good, and the first discharge capacity is $0.15\text{mA}\cdot\text{h} / \text{g}$ and $144.2\text{mA}\cdot\text{h} / \text{g}$ ($2.8 \sim 4.6\text{V}$ vs Li^+ / Li), The first charge and discharge efficiency was 51.8% and 58.1% respectively, and the capacity retention rates after 8 and 10 cycles were 92.4% and 78.5% respectively. The first discharge capacity of the Ti doped sample was $51.3\text{mA}\cdot\text{h} / \text{G}$, poor electrochemical performance.

KEYWORDS: lithium ion battery; doping type cathode material; layered $\text{Li}[\text{Ni}_{0.8-x}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Mx}]_2\text{O}_2$; coprecipitation method; preparation and performance.

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Preface

Energy crisis and the growing environmental pollution makes the world has set off a research and development of electric vehicles boom. Countries around the world use of clean energy vehicles (mainly to electric vehicles) attach great importance to invest a lot of money and manpower for research and development work. The development of electric vehicles around the world has achieved initial results. Power battery is the heart of electric vehicles. Lithium-ion battery with its many advantages had become scholars of various countries high competing. Lithium-ion battery because of its high energy, long life, low energy consumption, pollution-free, no memory effect and self-discharge, small internal resistance, cost-effective, less pollution, lithium-ion battery in the gradual application shows great advantages [1]. Also, it is expected to show good prospects in mobile phones, laptops, camcorders, digital cameras, electric vehicles, energy storage, aerospace and other fields [2-3].

Lithium-ion battery performance and lithium-ion battery material performance is closely related to the development of lithium-ion battery is always accompanied by the continuous improvement of battery materials and innovation. The current focus of lithium-ion battery research focused on the cathode material, anode materials and electrolyte materials and so on. The specific capacity of the cathode material is increased by 50% for every 50% of the specific capacity of the cathode material, and 50% for the specific capacity of the negative electrode material, and the power density of the battery will be increased by 13%. Therefore, the cathode material of lithium-ion battery plays a key role in the electrical performance of lithium-ion battery, which is the core material of lithium ion battery production. At present, the specific capacity of the anode material of lithium ion battery is twice that of the cathode material. The actual specific capacity of the cathode material has become the bottleneck restricting the development of lithium ion battery. Therefore, it is important to study the lithium ion battery cathode material for the development and improvement of lithium ion battery Practical significance. At present, the practical cathode material is mainly LiCoO_2 , LiNiO_2 , LiMn_2O_4 , but cobalt metal resources are scarce, expensive, and toxic will lead some pollution to the environment, so it cannot meet the requirements of large-scale power battery [4]. LiMn_2O_4 has the advantages of low cost and low cycle performance and

safety, and it is difficult to adapt to the needs of the next generation lithium ion battery. [5] LiMn_2O_4 has the advantages of low cost and low cycle performance and safety. In 1999, Liu et al reported the Ni-Cr-Mn ternary transition metal composite oxide of $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ ($0 < x < 0.5$, $0 < y < 0.5$), which was $\text{LiCoO}_2 / \text{LiNiO}_2 / \text{LiMnO}_2$ eutectic. It is considered to be one of the most promising LiCoO_2 cathode materials, which has good cycle performance of LiCoO_2 , high specific capacity of LiNiO_2 and the safety of LiMnO_2 . And this material reduces the amount of cobalt, reducing the cost of lithium-ion battery, while reducing the pollution of the environment [6].

As the layered nickel-cobalt-manganese ternary transition metal composite oxide cathode material is a powder material, the bulk density is closely related to the particle morphology, particle size and distribution of the powder. In addition, both the preparation method and the synthesis conditions have important influence on the structure, morphology and electrochemical properties of the lithium ion battery cathode materials. Therefore, the research on the layered nickel-cobalt-manganese ternary transition metal composite oxide. In the preparation of innovative methods, as well as in the surface modification, shape control, doping and applied to industrial production and other aspects of in-depth study [7-8]. In the preparation method, different calcination temperature and time have an important effect on the ordering degree of the cations, and the electrochemical properties of the materials will be different [9-10]. Therefore, people began to pay attention to Ni-Co-Mn ternary series of transition metal oxide in the application of lithium batteries [11-12]. In recent years, the research on lamellar lithium manganese oxide of doping type lithium ion battery cathode electrode has attracted people's attention. Doping is an important means to improve the performance of electrode material. In the modification of cathode material, widely used, the commonly used doping elements for the Mg, Al, Zn, Mo, Ti, La and F, the right amount of correct cation and cation doping can stabilize the structure of the material to improve the material recycling performance. The material based with better high current charge and discharge capacity [13-19].

In this paper, the precursors $\text{Ni}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ were prepared by hydrothermal coprecipitation. The precursors were treated with $\text{Mg}(\text{OH})_2 / \text{Zn}(\text{NO}_3)_2 / \text{TiO}_2$ and $\text{LiOH} \cdot \text{H}_2\text{O}$, Li_2CO_3 by $\text{Li} : \text{Ni} + \text{Co} + \text{Mn} : \text{Mg} / \text{Zn} / \text{Ti} = 1.06 : 0.96 : 0.04$. Li-Ni-ion battery layer $\text{Li}[\text{Ni}_{0.8-x}\text{Co}_{0.1}\text{Mn}_{0.1}\text{M}_x]\text{O}_2$ ($x = 0.04$) cathode material. The effects of synthesis conditions on the chemical properties of the composites were investigated. The synthesized samples were tested by scanning electron microscopy (SEM), thermogravimetric analysis (TG-DTG), X-ray diffraction (XRD) and constant current charge on discharge tests and characterization.

1. Experimental

1.1. Experimental apparatus and medicine

1.1.1 Experimental apparatus

DF-101B type heating thermostat heating magnetic stirrer (Gongyi City to China Instrument Co., Ltd.); 101-2AB type electric blast oven (Shanghai Liangping Instrument Co., Ltd.) (Tianjin Tesi Instrument Co., Ltd.); SGQ tube high temperature atmosphere furnace (Xiangtan City Zhongshan Instrument Factory); Super1220 / 750/900-super purification (Dainan Aolong Radiation Instrument Co., Ltd.); BK-6016A / 2mA rechargeable battery performance testing equipment (Guangzhou Blue Qi Electronic Industrial Co., Ltd.); Y2000-X-ray diffraction analyzer (Dandong Aolong Radiation Instrument Co., Ltd.) (Nanjing Changping Electronic Industrial Corporation); standard sieve (200) head (Zhejiang Shangyu); FEI QUANTA 200 Environmental Scanning Electron Microscope (US FEI); DTG-60AH (Shimadzu International Trade Shanghai Co., Ltd.).

1.1.2 Experimental drugs

(AR, Hunan Huiyong Reagent Co., Ltd.); $\text{LiOH} \cdot \text{H}_2\text{O}$ (AR, Tianjin Co., Ltd. (hereinafter referred to as 'Li₂O'), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (AR, Hengyang Kaixin Chemical Co., Ltd.) (AR), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR, Tianjin Ke Miou Chemical Reagent Co., Ltd.); $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (AR) (AR, Chengdu Kelon Chemical Reagent Factory); $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (AR, Tianjin Guangfu Technology Development Co., Ltd.); $\text{LiSO}_4 \cdot 6\text{H}_2\text{O}$ (AR, Guangdong Guanghua Chemical Co., Ltd.); Li_2CO_3 (AR, Chengdu Kelon Chemical Reagent Factory); NaOH (AR, Hunan Huiyong Reagent Co., Ltd.); TiO_2 (AR, Xiangzhong Fine Chemical Factory).

1.2. Experimental methods

1.2.1 Preparation of $\text{Ni}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ Precursor

$(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, manganese nitrate mixed solution (cation ratio $\text{Ni} : \text{Co} : \text{Mn} = 2$) was slowly added to the three-necked flask with constant temperature and constant stirring at 55°C . $0.76 : 0.1 : 0.1$) and $0.4 \text{ mol} / \text{L}$ $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution. After the dropwise addition, the pH of the reaction system was adjusted to $10 \sim 11$ with sufficient amount of 2

mol / L NaOH solution, nitrogen protection, reaction 10 h, vacuum filtration, washing to the filtrate pH of about 7, the precipitation in a vacuum oven at 110 °C for 10 h; weighing. To obtain Ni_{0.76}Co_{0.1}Mn_{0.1}(OH)₂ precursor.

1.2.2 Preparation of LiNi_{0.76}Co_{0.1}Mn_{0.1}Zn_{0.04}O₂

And a mixture of Zn(NO₃)₂ and a mixed amount of LiOH · H₂O and Li₂CO₃ powder (in the order of Li: (Ni + Co +)) were weighed in an agate mortar, Mn: Mg / Zn / Ti = 1.06: 0.96: 0.04 ingredients}, continue mixing in the agate mortar for half an hour to make it evenly mixed, and then mixed with a ball mill for 10 h (ball mass ratio 10: 1) Tablet. In the tube furnace at 450 °C for 5 h, heated to 900 °C constant temperature calcination 10 h or 20 h, the heating rate of 5 °C / min. After cooling at room temperature after 200 mesh sieve, that was products LiNi_{0.76}Co_{0.1}Mn_{0.1}Zn_{0.04}O₂.

LiNi_{0.76}Co_{0.1}Mn_{0.1}Mg_{0.04}O₂ and LiNi_{0.76}Co_{0.1}Mn_{0.1}Ti_{0.04}O₂ were prepared by the same method using Mg(OH)₂ and TiO₂ raw materials respectively.

1.3. Characterization of materials

1.3.1 X-ray diffraction (XRD)

The samples were analyzed by Y-2000A X-ray diffraction (XRD) analyzer (Dandong Aolong Radiation Instrument Co., Ltd.). The test conditions were as follows: CuK α radiation, 30 KV, 50 mA, step width 0.02, scanning speed 2 / Min, scanning range (2 θ) is 10-90 o.

1.3.2 Hot and Differential Thermal Analysis (TG-DTA)

The temperature of the mixed powder was 30 °C -900 °C, the heating rate was 10 °C · min⁻¹, and the protective atmosphere was the air atmosphere.

1.3.3 Electrochemical Impedance Spectroscopy (EIS)

The impedance characteristics of the electrode materials synthesized by different methods were tested by AC impedance method. The experiment was carried out on the CHI660C electrochemical workstation workstation manufactured by Shanghai Chenfang Instruments. The amplitude of the AC excitation signal was 5 mv and the frequency range was 10 mHz to 105 Hz. Experimental use of button cell system to the battery cathode termination of the electrode, the negative termination of the auxiliary electrode and the reference electrode, the AC impedance test.

1.3.4 Scanning Electron Microscopy (SEM)

The experiment was carried out on a Quata200 environmental scanning electron microscope manufactured by FEI with an acceleration voltage of 20 KV, a Spotsize of 3.5, and a resolution of 2-3 nm.

1.3.5 Electrochemical performance test

A mixture of 90% of the positive electrode active material and 3% of the carbon black conductive agent was added with 7% polyvinylidene fluoride (PVDF) and an appropriate amount of N-methylpyrrolidone (NMP) (the amount of NMP was uniform Coated in the agate mortar into a paste into the paste, evenly coated on 0.3 ~ 0.35mm aluminum foil, dried in a common oven at 125 °C for 25 min, and then dried in a vacuum oven at 110 °C 10 (EC) -dimethylcarbonate (DMC) -ethyl (1-methyl-2-hydroxyphenyl) -dimethylsilate (DMC) in the vacuum glove box was used to prepare the working electrode. Methyl carbonate (1: 1: 1, mass ratio) assembled into R2025 type button cell.

Battery charge and discharge performance test: CC-CV mode, rechargeable battery performance testing equipment (BK-6016A / 2, Guangzhou Blue Qi Electronic Industrial Co., Ltd.) charge and discharge cycle. The cycling conditions were: 14 mA · g⁻¹, 2.8-4.6 VvsLi / Li⁺, 25 °C (140 mA · g⁻¹ 0.1 °C). Such as the first charge and discharge cycle of the battery charge cycle mode 0.1 C constant current charge to 4.4VvsLi / Li⁺ constant voltage charging to the lower limit current of 0.02 mA, and then shelved 10 min, then 0.1 times constant current discharge to the lower limit voltage 2.8 Vvs Li / Li⁺ The The battery was subjected to a cycle life test in the same manner, but the constant current density of the battery was changed to 0.2 C magnification.

2. Results and discussion

2.1. TG-DTG analysis

In order to study the reaction mechanism of the mixture after the lithium-doped mixture in the heat treatment and the temperature range of the $\text{LiNi}_{0.8}\text{XCo}_{0.1}\text{Mn}_{0.1}\text{MXO}_2$ phase, the heat treatment is carried out reasonably, and the precursor $\text{Ni}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}$ is prepared. $\text{Ni}(\text{OH})_2$ and Li_2CO_3 , $\text{LiOH} \cdot \text{H}_2\text{O}$, TiO_2 were mixed and the powder was subjected to differential thermal analysis. The temperature range was $0 \sim 900^\circ\text{C}$. Fig.1 shows the TG-DTG curve of the mixture of $\text{Ni}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ and Li_2CO_3 , $\text{LiOH} \cdot \text{H}_2\text{O}$ and TiO_2 . It can be seen from the figure that the TG curve has three The weight loss rates on the TG curve were 26%, 15% and 3%, respectively, at $70 \sim 130^\circ\text{C}$, $275 \sim 325^\circ\text{C}$, $695 \sim 705^\circ\text{C}$, respectively. The corresponding DTA curve near the temperature (from the figure should be 105°C , 280°C and 700°C near) endothermic peak. Comparison of the differential thermal analysis of the prepared precursors $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ and $\text{LiOH} \cdot \text{H}_2\text{O}$ mixed powders [10]. It is presumed that at $70 \sim 130^\circ\text{C}$, the adsorption of water on the surface of the precursor and desorption of lithium hydroxide adsorbate with lithium hydroxide lithium carbonate. With the increase of temperature, there is a slow weight loss process at $275 \sim 325^\circ\text{C}$, which may be $\text{Ni}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ at $695 \sim 705^\circ\text{C}$, this time should be $\text{Ni}(\text{superscript } 2+)$, $(\text{OH})_2$ and Li_2O , TiO_2 are gradually combined to form $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Ti}_{0.04}\text{O}_2$.

It can be seen from Fig. 1 that the reaction of Li_2CO_3 , $\text{LiOH} \cdot \text{H}_2\text{O}$, TiO_2 and $\text{Ni}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ is decomposed by the dehydration process and the reaction is carried out because the reaction of the system is carried out with increasing temperature Melting is a slow process, so the temperature should not be too fast. Li_2CO_3 , $\text{LiOH} \cdot \text{H}_2\text{O}$, TiO_2 are completely melted and decomposed and fully penetrated into the ternary material, and the contact is more uniform, which is beneficial to the crystal development and improve the electrochemical performance of the product.

Figure 1. TG-DTG curve of $\text{Ni}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2\text{-Li}_2\text{CO}_3 / \text{LiOH} / \text{TiO}_2$ system

2.2. XRD analysis of samples

2.2.1 900°C 10 h roasting sample $\text{LiNi}_{0.8}\text{XCo}_{0.1}\text{Mn}_{0.1}\text{MXO}_2$ XRD analysis

Figure 2 shows the XRD pattern of $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Mg}_{0.04}\text{O}_2$ and $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Zn}_{0.04}\text{O}_2$ samples after pretreatment at 450°C for 5 h at 900°C for 10 h. The spectra are shown in the literature [15] The spectra of $\text{LiNi}_{1/3}\text{XCo}_{1/3}\text{Mn}_{1/3}\text{2xMoX O}_2$ ($x = 0.01, 0.02, 0.05$) are very similar. The synthesized samples have typical $\alpha\text{-NaFeO}_2$ structure, which belongs to space group and hexagonal system. It can be seen from Figure 2 that $\text{LiNi}_{0.8}\text{XCo}_{0.1}\text{Mn}_{0.1}\text{MXO}_2$ exhibits a higher diffraction peak at about $2\theta = 18.8^\circ$ due to the diffraction peaks of transition metals Ni, Co and Mn oxides. (108) / (110) splitting bimodal in the XRD curves of all samples, and (006) / (102) splitting bimodal is less obvious, indicating that LiNiO with lamellar structure is synthesized under this condition $.8\text{-XCo}_{0.1}\text{Mn}_{0.1}\text{MXO}_2$ sample. Hu Zhengyue et al. [17] studied the degree of cationic mixing of I003 / I104 with the peak intensity ratio of I003 / I104. When the ratio of I003 / I104 was greater than 1.2, the smaller the degree of cationic mixing was, the material had a good lamellar structure. The calculated results show that the I003 / I104 data of the doped sample (Mg / Zn) are 0.53 and 0.97 respectively when the calcination temperature is 900°C and the calcination time is 10 h, which is obviously less than 1.2, respectively. At 900°C temperature The lamellar structure of the 10h synthetic sample is poor. In addition, R-factor $R = (\text{I}102 + \text{I}006) / \text{I}101$ can represent hexagonal lattice order, R value is smaller, then hexagonal lattice order better. The R value of the doped samples (Mg / Zn) synthesized at 900°C for 3 h is 2.798, 1.511, and the apparent ratio is too large. This further shows that the layered structure of the samples synthesized at 900°C for 10 h is not enough it is good.

Figure 2. XRD patterns of samples calcined at 900 °C for 10 h: a, $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Zn}_{0.04}\text{O}_2$; b, $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Mg}_{0.04}\text{O}_2$

2.2.2 900 °C 20h calcination sample $\text{LiNi}_{0.8}\text{XCo}_{0.1}\text{Mn}_{0.1}\text{MXO}_2$ XRD analysis

Figure 3 shows the XRD patterns of $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Mg}_{0.04}\text{O}_2$, $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Zn}_{0.04}\text{O}_2$, $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Ti}_{0.04}\text{O}_2$ samples after pretreatment at 450 °C for 5 h and calcined at 900 °C for 20 h. The spectrum is very similar to the XRD pattern of $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.1}\text{O}_2$ prepared by Cheng Guixia et al. [10]. According to the analysis of Fig. 3, it can be seen that there are obvious peaks (006) / (102) and (108) / (110) splitting bifurcations in the XRD curves of all the samples, indicating that the samples with the layered structure. The calculation of I003 / I104 data shows that the I003 / I104 data of the doped sample (Mg / Zn / Ti) are 1.39, 1.26, 1.48, which is obviously larger than 1.2 when the calcination temperature is 900 °C and the calcination time is 20 h. The larger the mixing degree of the cation, the smaller the mixing degree of the cation is, indicating that the synthesized sample has a better lamellar structure, which is consistent with the presence of (006) / (102) and (108) / (110). (Mg / Zn / Ti) were 0.497, 0.603, 0.555, respectively, which indicated that the calcination time at 900 °C was 20 h. The samples were prepared at 20 °C for 20 h at 900 °C for 20 h. Has a good hexagonal lattice order. (006) / (102) and (108) / (110) splitting bimodal peaks in I003 / I104 data, R data and XRD curves can be considered to be calcined at 900 °C for 20 h. $\text{LiNi}_{0.8}\text{XCo}_{0.1}\text{Mn}_{0.1}\text{MXO}_2$ powder phase structure is better.

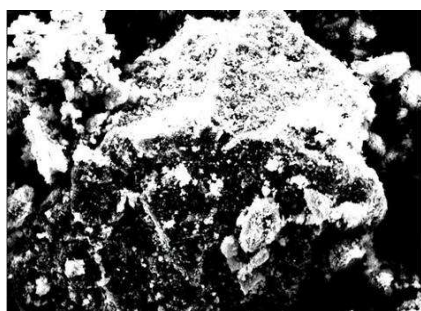
The samples were calcined at 900 °C for 10 h and 20 h after pretreatment at 450 °C for 5 h. It was found that the samples were calcined at 900 °C for 10 h (108) / (110) split bimodal, but (006) / (102) and the I003 / I104 data were small, and the diffraction peaks at 900 °C for 20 h were sharp, and the peaks were in accordance with the hexagonal characteristics. The synthetic materials belonged to the $\alpha\text{-NaFeO}_2$ layered structure. The (108) peak (110) peak is also obvious, the cationic mixing degree is small, and no impurity peaks appear, the product samples show obvious lamellar features, different time calcination. Of the two types of samples are clearly different, and this difference is the result of two types of samples of the most direct reason for the difference in electrochemical performance.

Figure 3. XRD pattern of 20 h sample calcined at 900 °C: a. $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Ti}_{0.04}\text{O}_2$; b. $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Zn}_{0.04}\text{O}_2$; c. $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Mg}_{0.04}\text{O}_2$.

2.3. SEM analysis of samples

Fig. 4 is a SEM image of $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Zn}_{0.04}\text{O}_2$ calcined at $900\text{ }^\circ\text{C}$ for 20h. Figure 4 (a) is magnified 2000 times the sample of the SEM, we can see the product particle size of about $40\mu\text{m}$ particles, the particle shape is not regular (or spherical), poor mobility, there is a small grain agglomeration phenomenon, The secondary particles of the aggregates are not uniform in size, and the agglomeration phenomenon will not be beneficial to the doping and deintercalation reactions of dopant ions and lithium ions, and the materials will not have good electrochemical performance. Due to the irregular shape of the particles, its expansion and ductility is poor, and mixed with other materials show poor miscibility, so the resulting product processing performance is poor, is not conducive to the production of cathode material slurry and electrode the coating of the sheet makes the quality of the electrode sheet not high. Figure 4 (b), the spherical particles are essentially irregular spherical particles with a particle size of 3 to $4\mu\text{m}$, and it is found that the surface of the individual particles is not sufficiently smooth, and these are small Crystal development is not complete, the crystallinity is not high enough.

Fig. 5 is a SEM image of $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Mg}_{0.04}\text{O}_2$ calcined at $900\text{ }^\circ\text{C}$ for 20 h. From Figure 5 (a) is a magnification of 5000 times the sample SEM image, we can see that the product is about $5\mu\text{m}$ particle size, the particle shape of irregular lumps, and there are small particles agglomeration phenomenon. However, this agglomeration phenomenon is weakened, and the intercalation and desorption reactions of dopant ions and lithium ions will be beneficial, so the electrochemical properties of the materials will be better. (B), it was found that the surface of the sample was relatively smooth and the particle size was about $3\mu\text{m}$. The crystal development of these primary grains was relatively complete and the crystallinity was higher. There is a large gap between the small grains, which is conducive to the penetration of the electrolyte inside the material, thereby improving the utilization of the cathode material.

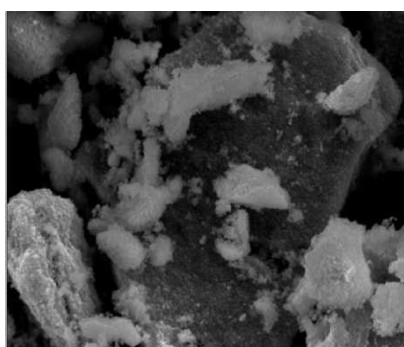


(A) x2000

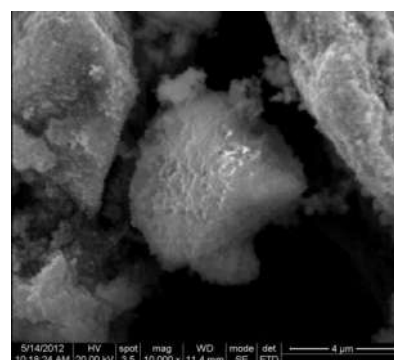


(b) x10000

Figure 4. $900\text{ }^\circ\text{C}$ calcined 20 h sample $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Zn}_{0.04}\text{O}_2$ SEM



(A) x5000



(b) x10000

Figure 5. $900\text{ }^\circ\text{C}$ calcined 20 h sample $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Mg}_{0.04}\text{O}_2$ SEM

Figure 4 and Figure 5 can be seen by $\text{Ni}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ and Li_2CO_3 , $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$ mixed powder through the sintering of the product $\text{LiNi}_{0.76}\text{Co}_{0.1}\text{Mn}_{0.1}\text{Mg}_{0.04}\text{O}_2$ do The battery material is relatively good, the crystal is more perfect, but relative to Wang Ximin et al [8] prepared $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ particle shape is also less regular.

2.4. Electrochemical energy analysis

From the XRD analysis of 2.2 samples, it can be seen that the sample calcined at 900 °C for 10 h cannot be used as the ideal cathode material because of its composition and structure, and the electrochemical performance of the sample is only 20 °C for 20 h.

In order to study the effect of doping elements on the electrochemical properties of the materials, the materials were assembled into batteries and charged and discharged at 0.1 C and 2.8 ~ 4.6 V. Fig.1 The first charge-discharge curve of LiNi_{0.8-x}Co_{0.1}Mn_{0.1}MXO₂ prepared by calcination at 20 °C for 20 h at different temperatures (Mg / Zn / Ti) at 900 °C. It can be seen from Fig. 6 that the first charge capacity of Mg-doped material is 230.9 mA.h / g, the discharge capacity is 119.5 mA.h / g, the irreversible capacity is 111.4 mA.h / g, the discharge efficiency is 51.8%. The discharge capacity is 144.8 mAh · g⁻¹, the irreversible capacity is 104.0 mAh · g⁻¹, the discharge efficiency is 58.1%; the first charge capacity of Ti doped material is 264.3 MAh · g⁻¹, the discharge capacity is only 53.2 mAh · g⁻¹, the irreversible capacity is 211.1 mAh · g⁻¹, and the discharge efficiency is 20.1%. (M = Co, Al, Ti; x = 0, 0.025) prepared by the method described by the following formula: (18) Li ((Ni_{0.5-x}Mn_{0.5-x}M_{2x}), Al, Ti, and the doping amount of 5%, respectively, were 140 mAh · g⁻¹, 142 mAh · g⁻¹, and 132 mAh · g⁻¹, respectively. And the first discharge capacity of Zn material is higher, the irreversible capacity is much lower than that of Ti doped material, and the charge and discharge efficiency is relatively high.

Figure 6. 900oC calcination 20 h material of the first charge and discharge curve

Figure 7. 900oC calcined 20 h material AC impedance diagram

In order to have a reasonable explanation of the above results, the AC impedance of the sample after the first cycle is tested. As a result, as shown in Fig. 7, each material has only one obvious semicircle, possibly because the interface reacts with the electrochemical reaction. The frequency range is overlapped and integrated into a semicircle. The interfacial reaction and electrochemical reaction impedance of LiNi_{0.76}Co_{0.1}Mn_{0.1}M_{0.04}O₂ doped with Mg and Zn and Ti at 20 °C for 20 h were 590 Ω, 110 Ω, 320 Ω which is beneficial to the solid phase diffusion and electrochemical reaction of ions.

As shown in Table 1, the first discharge capacity, the first charge / discharge efficiency, and the first cycle AC impedance data of LiNi_{0.8}-XCo_{0.1}Mn_{0.1}MXO₂ material with different doping (Mg / Zn / Ti) 900 °C calcination for 20 h are listed. We can clearly understand the data, different doping elements of its first discharge capacity, the first charge and discharge efficiency, the first cycle of AC impedance have an impact, and a greater impact. By comparing the data, we can see that the first discharge capacity and the first charge / discharge efficiency of the Mg and Zn doped materials are much better than those of Ti doped materials.

Table 1 LiNi_{0.8}-XCo_{0.1}Mn_{0.1}MXO₂ material for 20 h calcination at 900 ° C for different doping (Mg / Zn / Ti) First charge and discharge data (0.1C magnification)

Doping elements	Initial discharge capacity l / mAh g -	First discharge efficiency / %	First cycle impedance / Ω
Mg	119.5	51.8	590
Zn	144.2	58.1	110
Ti	53.2	20.1	320

Based on the above analysis, the results of SEM.XRD and the electrochemical properties of the three different doping elements were compared. It was found that after pretreatment at 450 °C for 5 h, the contents of LiNi_{0.76}Co_{0.1}Mn_{0.1}Zn_{0.04}O₂ and LiNi_{0.76}Co_{0.1}Mn_{0.1}Mg_{0.04}O₂ have better chemical properties, while LiNi_{0.76}Co_{0.1}Mn_{0.1}Ti_{0.04}O₂ has poor chemical properties.

Figure 8 900°C roasting 20 h material battery cycle life curve

In order to further study the influence of electrochemical stability of different dopant materials, the electrochemical cycling of LiNi_{0.76}Co_{0.1}Mn_{0.1}Zn_{0.04}O₂ material and LiNi_{0.76}Co_{0.1}Mn_{0.1}Mg_{0.04}O₂ was carried out. The loop diagram is shown in Figure 8. It can be seen from Figure 8 that the sample with Mg doped at 900 °C for 20 h has good cycle performance, and the capacity is reduced by 8.4 times, the retention rate is 92.4%, and the electrochemical performance is better. 900 °C sintering 20 h doped Zn material recycling performance is relatively poor, 10 times after the cycle, the capacity of more attenuation, the retention rate of only 78.5%. The mechanical properties of Mg doped with 900 °C sintered at 20 °C for 20 h were the best, and the mechanical properties of Mg were the best.

3. Conclusions

(1) The precursor Ni_{0.76}Co_{0.1}Mn_{0.1}(OH)₂ was prepared by hydrothermal coprecipitation method. LiNi_{0.76}Co_{0.1}Mn_{0.1}Mg_{0.04}O₂ was synthesized by high temperature solid phase method. The sintering conditions were investigated the effect of Miscellaneous Elements on Product Performance. XRD results show that the sample structure of the samples synthesized at 900 °C for 20 h is obviously 1. The calculated data of the I003 / I104 of the doped samples (Mg / Zn / Ti) are 1.39, 1.26, 1.48 and the R values are 0.497, 0.603 and 0.555 respectively; TG / DTG analysis shows that Li₂CO₃, LiOH · H₂O, TiO₂ can be completely melted and decomposed and fully penetrated into the ternary material, so that the mixing is more uniform, which is beneficial to the crystal development and improve the product Of the electrochemical properties. The results show that the particle size of LiNi_{0.76}Co_{0.1}Mn_{0.1}Mg_{0.04}O₂ is more uniform by the sintering of Ni_{0.76}Co_{0.1}Mn_{0.1}(OH)₂ and Li₂CO₃, LiOHH₂O, Mg(OH)₂, Shape more rules, more perfect crystal.

(2) The results show that the types of doping elements have a significant effect on the performance of the battery material, and the LiNi_{0.76}Co_{0.1}Mn_{0.1}Mg_{0.04}O₂ material and the doped element (Mg / Zn / Ti) are calcined at 20 °C for 20 h for the first time The discharge capacity was 119.5 mA.h / g / 144.2 mA.h / g / 51.3 mA.h / g (2.8 to 4.6 V, 0.1

C magnification) and the doped element (Mg / Zn / Ti) Of the AC impedance values were 590 Ω , 110 Ω , 320 Ω , which may be due to different doping elements, the obtained electrode material structure and particle morphology caused by different.

(3) The discharge capacity of the doped element (Mg / Zn) with higher discharge capacity was 115.15 mA.h / g and 91.81 mA.h / g, respectively, after 8 times and 10 times of 0.2C cycles. Respectively, the first discharge capacity of 91.9%, 78.7%), indicating that the sample cycle performance is relatively good.

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