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Research on Preparation and Electrochemical Performance of the High Compacted Density Ni-Co-Mn Ternary Cathode Materials

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Abstract

The high compacted density $LiNi_{0.5-x}Co_{0.2}Mn_{0.3}Mg_xO_2$ cathode material for lithium-ion batteries was synthesized by high temperature solid-state method, taking the Mg element as a doping element and the spherical $Ni_{0.5}Co_{0.2}Mn_{0.3}(OH)_2$, Li_2CO_3 as raw materials. The effects of calcination temperature on the structure and properties of the products were investigated. The structure and morphology of cathode materials powder were analyzed by X-ray diffraction spectroscopy (XRD) and scanning electronmicroscopy (SEM). The electrochemical properties of the cathode materials were studied by charge-discharge test and cyclic properties test. The results show that $LiNi_{0.4985}Co_{0.2}Mn_{0.3}$ $Mg_{0.0015}O_2$ cathode material prepared at calcination temperature 930˚C has a good layered structure, and the compacted density of the electrode sheet is above 3.68 g/cm^3. The discharge capacity retention rate is more than 97.5% after 100 cycles at a charge-discharge rate of 1C, displaying a good cyclic performance.

Keywords

High Compacted Density, Ternary Cathode Materials, Electrochemical Performance

1. Introduction

Li-ion batteries (LIBs) have been widely used in portable electronic devices and electric vehicles due to their high specific energy, cyclic stability, and low environmental pollution [1] [2]. Especially, Nickel-cobalt-manganese ternary ca-

thode material has become the largest incremental LIBs cathode material in the global market due to its advantages of high specific capacity. In recent years, the demand for energy density has gradually increased, so the focus of cathode material is on the nickel-rich ternary material, high voltage ternary material and high compacted density ternary material [3]. In applications, such as in the new energy vehicle market, high-nickel multi-element cathode materials and high voltage ternary materials are gradually improving their price/performance ratio by increasing their nickel content while reducing their cobalt content. However, they still face challenges, such as poor structural stability, surface microcracks and particle fragmentation, rapid decay in cycle life, poor thermal stability, and poor safety performance [4]-[12]. In addition, since the structure of spherical particles, namely the secondary particles, is inevitably fractured during the electrode rolling and the repetitive lithiation/delithiation process as a result of transient diffusion. Compared with the single crystal large particles of lithium cobalt oxide material, the ternary cathode material belongs to the small agglomerates (≤0.5 μm), the compacted density (≤3.5 g/cm^3) is lower, and the energy density cannot be effectively improved. Thus, it is of significance to understand the inner structures of agglomerates.

In this study, the inner structure of agglomerates is investigated, which refers to the arrangement of plate-like primary particles in the secondary particles. The Nickel-cobalt-manganese ternary cathode material with a larger size of the inner structure of agglomerates (~2 μm) is prepared, which can not only enhance the density of the secondary spherical particles, but also improve the compaction density (~3.70 g/cm^3). Therefore, the larger size of the inner structure of agglomerate has a more complete crystal structure, showing a better electrochemical performance.

2. Experimental

Synthesis of Materials. The spherical precursor $Ni_{0.5}Co_{0.2}Mn_{0.3}(OH)_2$ was synthesized by a modified co-precipitation method. Briefly, proper amounts of $NiSO_4$, $CoSO_4$ and $MnSO_4$ (cationic ratio of Ni:Co:Mn = 5:2:3) were added to a strongly stirred tank reactor under nitrogen atmosphere, forming 2.0 mol·L^{-1} solution. 4.0 mol·L^{-1} NaOH solution and 2.0 mol·L^{-1} ammonia were added at the same time. The obtained precursor was then dried at 100˚C for 12 h in the air. After drying, the precursor and Li_2CO_3, MgO were ball milled for 6 h. The Li/TM molar ratio was fixed at 1.05. Meanwhile, Mg element at 0%, 0.10%, 0.15%, 0.20%, 0.25% stoichiometric ratio was added. The cathode material was heated to 500˚C at a rate of 3˚C/min, then to 900˚C at a rate of 2˚C/min and finally calcined for 12 h. For comparison, the different samples were heated to 910˚C, 920˚C at a heating rate of 2˚C/min, respectively. Three cathode materials were denoted as NCM-1, NCM-2 and NCM-3.

The post-treated $LiNi_{0.5-x}Co_{0.2}Mn_{0.3}Mg_xO_2$ was pulped, filtered, washed, dried, broken and sieved under the solid-liquid ratio (1:5); After sifting, $LiNi_{0.5-x}Co_{0.2}Mn_{0.3}Mg_xO_2$ was heated to 910˚C at a rate of 2˚C/min and finally calcined for 8

h. By comparison, the different samples were heated to 930˚C, 950˚C at a heating rate of 2˚C/min and finally calcined for 8h, respectively. Three cathode materials were denoted as NCM-4, NCM-5 and NCM-6. The powder with high pressure solid density was obtained by air flow crushing.

Materials Characterization. The particle size distribution was measured on a laser diffraction instrument (Malvern Mastersizer 3000, Malvern, UK) with dynamic light scattering methods. The sample structures were identified by using powder X-ray diffraction (XRD, Cu Ka radiation, Bruker D8 Advance). The morphology and element distribution were analyzed using a scanning electron microscope (SEM, JSM-6700F) equipped with an energy dispersive spectrometer (EDS, Horiba, EX-250). The metal ion content was determined by the inductively coupled plasma atomic emission spectrometry (ICP-AES).

Electrochemical Tests. The working electrode was prepared by mixing active materials ($LiNi_{0.5-x}Co_{0.2}Mn_{0.3}Mg_xO_2$, 85 wt%), carbon black conductive additive (Super P, 8 wt%), and polyvinylidene fluoride binder (PVDF, 7 wt%) dissolved in N-methylpyrrolidone (NMP). The slurry was then casted on aluminum foil and followed by drying at 120˚C for 24 h in vacuum oven. Electrolyte was a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing lithium hexafluorophosphate ($LiPF_6$) and Celgard 2400 film was used as separator. The cells were assembled in an argon-filled glove box with H_2O and O_2 concentrations below 0.1 ppm. All the electrochemical performances were performed on a LAND CT2001A (Wuhan, China) battery program-control test system between 3.0 and 4.3 V at different charge/discharge rate 0.2C/0.2C and 1C/1C (1C = 150 $mAh{\cdot}g^{-1}$) at 23 ± 2˚C.

3. Results and Discussion

3.1. Characterization of Physical Properties

Figure 1 shows the XRD patterns of three cathode samples, which corresponds to those with a-$NaFeO_2$ structure with the R3m space group.

The structural stability is closely related to "cation mixing", which means Ni^{2+} ions tend to migrate to Li^+ sites resulting in various problems including capacity

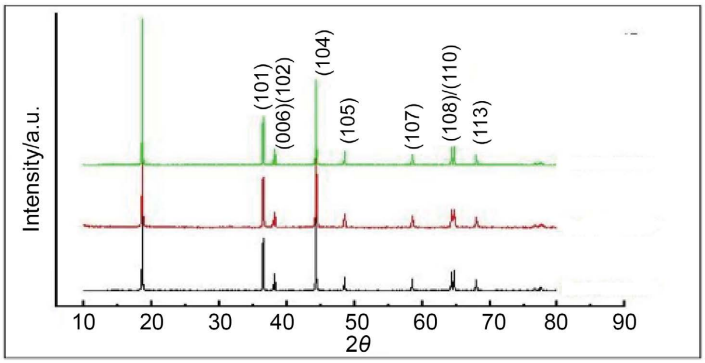

Figure 1. XRD patterns of $LiNi_{0.5-x}Co_{0.2}Mn_{0.3}Mg_xO_2$ cathode materials prepared at different calcination temperatures.

loss, structure deterioration and surface side reactions. Therefore, decreasing the degree of the disordering can originally reduce the performance degeneration and maintain the structural stability. Generally speaking, the intensity ratio of (003) to (104) peak ($I_{(003)}/I_{(104)}$) indicates the degree of cation mixing in the layered structure [13]. Previous result has shown that $I_{(003)}/I_{(104)}$ decreases as the degree of the disordering increases. Before cycling, the peak intensity ratios of $I_{(003)}/I_{(104)}$ are greater than 1.2 and the (006)/(102), (108)/(110) peaks of the three materials show obvious splits, indicating that the three materials have good layered structure. By comparison, The $I_{(003)}/I_{(104)}$ ratio of NCM-2 is much higher than the others in **Table 1**. It is evident that the crystal structure changes less and the structure is more ordered, which is conducive to Li^+ insertion/extraction. These results indicate that NCM-2 material has a good cycling performance (**Figure 2**).

SEM images of five $LiNi_{0.4985}Co_{0.2}Mn_{0.3}Mg_{0.015}O_2$ cathode materials after

Table 1. Lattice parameters of $LiNi_{0.5-x}Co_{0.2}Mn_{0.3}Mg_xO_2$ cathode materials prepared at different calcination temperatures.

Sample	$I_{(003)}/I_{(104)}$	R	a	c	c/a
NCM-1 (900˚C)	1.961	0.45	2.8747	14.1915	4.9367
NCM-2 (910˚C)	2.133	0.44	2.8761	14.1995	4.9369
NCM-3 (920˚C)	2.103	0.45	2.8750	14.1921	4.9363

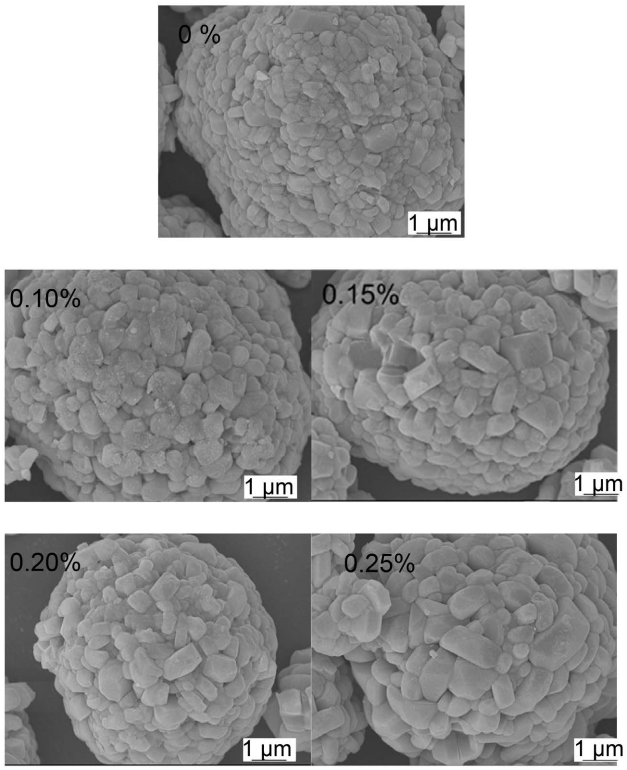

Figure 2. SEM images of $LiNi_{0.5-x}Co_{0.2}Mn_{0.3}Mg_xO_2$ cathode materials prepared at 910˚C.

slurrying treatment prepared at 910˚C, 930˚C and 950˚C calcination temperature heating rate of 2˚C/min and finally calcined for 8h are presented in Figure 3. With the increase of temperature, as a particle size increases gradually, $LiNi_{0.4985}Co_{0.2}Mn_{0.3}Mg_{0.015}O_2$ cathode material prepared at 930˚C has the best particle size, density of compaction and electrochemical performance.

3.2. Electrochemical Performance

Subsequent electrochemical measurements were carried out to evaluate the electrochemical performances. Charge-discharge performance was characterized at 0.2C in the voltage window of 3.0 - 4.3 V by button batteries. The cycle performances were characterized at 1C for 100 cycles in the voltage window of 3.0 - 4.3 V by cylindrical batteries.

The electrochemical performances of the three groups of ternary cathode materials are presented in Table 2. The first charge-discharge specific capacities of NCM-5 are 199.0 $mAh{\cdot}g^{-1}$ and 175.9 $mAh{\cdot}g^{-1}$. In contrast, the first discharge specific capacities of NCM-4 and NCM-6 cathode materials are 174.5 $mAh{\cdot}g^{-1}$ and 169.5 $mAh{\cdot}g^{-1}$, respectively. It can be seen that the NCM-5 cathode material shows higher capacity characteristics.

The results show that $LiNi_{0.4985}Co_{0.2}Mn_{0.3}Mg_{0.0015}O_2$ cathode material prepared at calcination temperature 930˚C has a good layered structure, and the compacted density of the electrode plate is above 3.68 g/cm^3. The discharge capacity retention rate is more than 97.5% after 100 cycles at a charge-discharge rate of

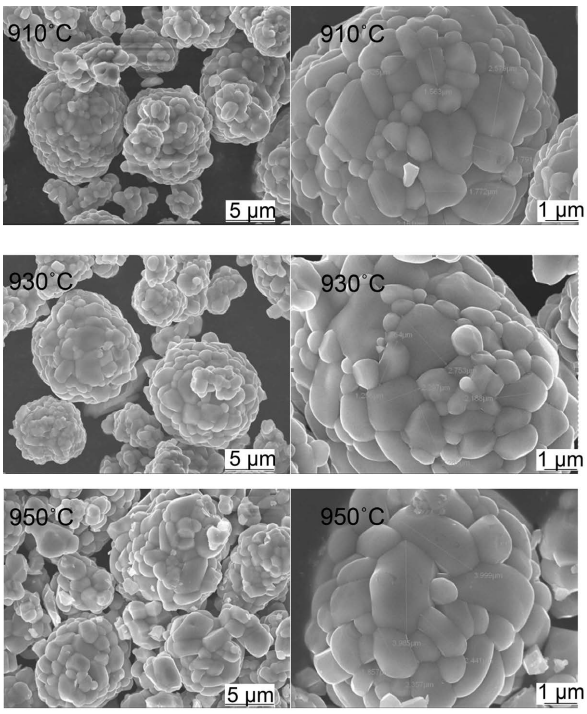

Figure 3. SEM images of $LiNi_{0.4985}Co_{0.2}Mn_{0.3}Mg_{0.015}O_2$ cathode materials taking the Mg element prepared at different calcination temperatures.

Table 2. Electrochemical performance of $LiNi_{0.4985}Co_{0.2}Mn_{0.3}Mg_{0.0015}O_2$ cathode materials prepared at different calcination temperature.

Sample	Specific capacity of initial charge (mAh/g)	Specific capacity of initial discharge (mAh/g)	Coulombic efficiency (%)
	CR2025, 3.0~4.3 V, 0.2C, 25˚C		
NCM-4 (910˚C)	200.0	174.5	87.2
NCM-5 (930˚C)	199.0	175.9	88.4
NCM-6 (950˚C)	198.2	169.5	86.4

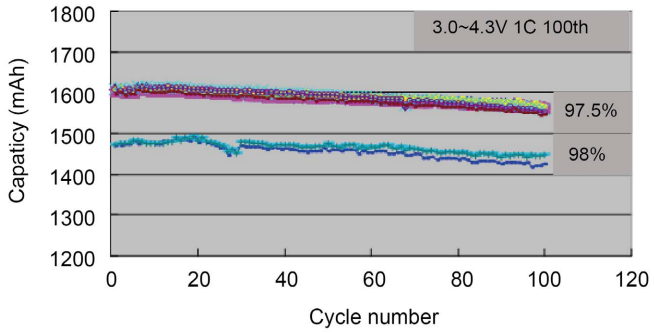

Figure 4. Cycling performance curves of $LiNi_{0.4985}Co_{0.2}Mn_{0.3}Mg_{0.0015}O_2$ cathode material.

1C, which shows a good cyclic performance. The results are in good agreement with XRD results (**Figure 4**).

4. Conclusion

In this paper, the high compacted density $LiNi_{0.4985}Co_{0.2}Mn_{0.3}Mg_{0.0015}O_2$ cathode material for lithium-ion batteries has been prepared. XRD results reflect that the cathode material shows good crystallinity and layered structure. SEM reveals that the cathode material delivers good sphericity and concentrated particle size distribution. The compacted density of the electrode plate is above 3.68 g/cm^3. Electrochemical tests show that it exhibits a better cycle performance of more than 97.5% capacity retention after 100 cycles at 1C.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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