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Structure and Electrochemical Performance of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ Cathode Materials Fabricated by Different Synthesis Methods

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LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode materials were synthesized by the solid-state method, Pechini method and co-precipitation method, respectively. The sample prepared by the co-precipitation method had the lowest cation mixing degree of Li⁺/Ni²⁺ and the best electrochemical properties among the materials prepared by these methods. Its maximum discharge capacity was 165.9 mAh g⁻¹ at the rate of 1 C, and the capacity retention rate was 75.4 % after 50 charge/discharge cycles. In addition, it demonstrated the best rate capacity of 116.7 mAh g⁻¹ at 5 C. The excellent cyclic stability and rate performance can be attributed to the stable crystal structure and minimal electrode polarization during the deintercalation/intercalation process of lithium ions.

Keywords: lithium-ion battery, cathode material, co-precipitation method, electrochemical performance

1. INTRODUCTION

Traditional fuels such as oil and coal are being depleted, and their combustion has led to serious environmental hazards. In recent years, some renewable natural energy sources, such as solar, wind and tidal energy, have received great attention in their harvesting and storage [1]. Rechargeable lithium-ion batteries (LIBs) have become one of the mainstream energy storage devices due to their high energy/power density, long cycle life and environmental friendliness, and are suitable for applications including consumer electronics, hybrid/all-electric vehicles, utility power grids and so on. [2]. The performance and applicability of these energy storage devices are highly dependent on the electrode materials, and therefore a great deal of research in the battery field has focused on improving the

performance of cathode materials to meet high capacity and fast charge/discharge rates [3]. The spinel structured LiM₂O₄, Olivine structured LiMPO₄ and layered-structured LiMO₂ (M is a three-dimensional transition metal, like Ni, Co, Mn, and Al, which and also can be a mixture of transition metals) are commonly used as cathode materials in LIBs [1]. LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM) cathode material is isostructural with LiCoO₂ but the concentration of Co is only 1/3 of that in LiCoO₂. In addition, the ternary NCM combines the advantages of Ni, Co, and Mn ions: Ni determines the capacity of the cathode; Co is responsible for the charge and discharge kinetics; and Mn maintains the structural stability of the material during the cycling process [4]. Multi-element NCM cathode materials are promising alternatives to LiCoO₂ due to their high capacity, high energy density, superior thermal stability, and especially their lower cost and less toxicity [2].

The NCM material combines the three elements of Ni, Co and Mn. Since the ionic radii of Ni²⁺and Li⁺ are similar, it is easier to produce cation mixing between Ni²⁺and Li⁺ during the preparation of this material, which leads to the disorder of the lattice structure and reduces the diffusion ability of Li⁺ as well as the discharge capacity of the battery [5]. Layered NCM cathode materials with good crystallinity were prepared by hydrothermal method by Wu et al [6]. The large $I_{(003)}/I_{(104)}$ ratio implies that less cation mixing occurs between Li and Ni ions, but the synthesis process is more complicated. 1D Nb-doped NCM nanofibers were prepared by electrospinning method by Lv et al. [7]. It was found that the cation mixing was alleviated by doping Nb^{5+} in a proportion of 2%. However, this increases the difficulty and cost of preparation, which makes it difficult to be applied in practice. It has been confirmed that cation mixing is the main cause of poor electrochemical performance, including structural degradation and capacity loss, surface side reactions, and poor thermal stability [7, 8]. Meanwhile, the physical properties of the cathode materials synthesized by different methods are different, which have a direct impact on the electrochemical performance of LIBs [9]. Therefore, from the perspective of practical applications, it is necessary to clarify the relationship between different preparation methods and synthetic parameters on the structure and electrochemical performance of NCM materials in order to better promote the industrialization of LIBs. In this work, NCM cathode materials were prepared by solid-state method, Pechini method and co-precipitation method, respectively, and their structural and electrochemical properties were compared.

2. EXPERIMENTAL

2.1 Materials synthesis

Li(CH₃COO)·2H₂O (AR, 99%), Ni(CH₃COO)₂·4H₂O (AR, 99%), Co(CH₃COO)₂·4H₂O (AR, 99%) and Mn(CH₃COO)₂·4H₂O (AR, 99%) were used as raw materials to prepare NCM cathode material by solid-state method. First, the corresponding acetates were weighed in the stoichiometric ratio of Li : Ni : Co : Mn=3.05:1:1:1 and grounded in a mortar until well mixed (5 % excess in molar ratio was kept to compensate for the volatilization of Li during the calcination) [10]. Then acetate mixture was placed in a muffle furnace to pre-react at 450 °C for 5 hours. Thereafter, the pre-fired powder was ground again and transferred to a muffle furnace for calcination at 850 °C for 10 hours. The target

product was obtained after cooling. In the experiments, the heating rate of the pre-firing and calcination was 5 $^{\circ}$ C per minute.

The Pechini method for the synthesis of NCM cathode is based on three consecutive reactions: complexation, lipidation and polymerization [11]. In this method, the same raw materials as in the solid-state method were used and dissolved in an appropriate amount of deionized water with the stoichiometric ratio of Li : Ni : Co : Mn=3.05:1:1:1. The citric acid was dissolved in ethylene glycol (molar ratio of citric acid to ethylene glycol is 1:4) and prepared with an appropriate amount of deionized water to form a mixed solution with the pH of about 1.5. The mixture of metal acetates was added dropwise to the above mixture at 100 °C with continuous stirring. At this time, the transition metal cations reacted with the oxygens on the divalent citrate ionized from citric acid to form complexes. Then the viscous mixture obtained by the reaction was then dried in a blast oven at 150 °C for 24 hours. At the beginning of the drying process, the complexes were polymerized together by glycols and undergo a lipidation reaction to remove small molecules of water to form a spatially structured gel. With further drying, excess ethylene glycol was removed and polymerization reactions took place to form polymers. Finally, the dried sample was ground and decomposed in a muffle furnace at 300 °C for 2 hours. After grinding again, the reaction was carried out at 850°C for 10 hours to obtain the final product.

The co-precipitation method is a two-step method in which the transition metal ions are precipitated first and then the lithium source is added for high temperature reaction. The NCM material prepared by this method has uniform particle size and is the most commonly used method for preparing ternary cathode materials in the market today. In this procedure, the oxalate co-precipitation method was used, and transition metal sulfates with good solubility were used as raw materials. The analytical grade chemicals NiSO₄·6H₂O, CoSO₄·7H₂O, and MnSO₄·H₂O with molar ratio of 1:1:1 were dissolved in deionized water under continuous magnetic stirring, and the concentrations of the solutions were adjusted to 2 mol L⁻¹. Meanwhile, the corresponding molar ratio of C₂H₂O₄·4H₂O was dissolved in deionized water, and the pH of the oxalate solution was adjusted to 8.5 by adding an appropriate amount of ammonia. Then the transition metal sulfate solution was added dropwise to the above solution at a certain rate with vigorous stirring. Afterwards, stirring was maintained at 50 °C for 4 hours. The precipitate was allowed to age for 5 hours after completion of the reaction. Then the precursor was obtained by centrifugation, washing, and drying of the precipitate. The precursor was mixed with excess LiOH·H₂O and ground well, then pre-fired at 500 °C for 5 hours. After cooling, the above reactants were ground again and calcined at 850 °C for 12 hours to obtain the desired NCM powder. The samples synthesized by the solid-state method, Pechini method and co-precipitation method were labeled as S1, S2 and S3, respectively.

2.2 Materials characterization

The precursors were analyzed by thermogravimetry-differential scanning calorimetry (TG-DSC) using a simultaneous thermal analyzer (Netzsch STA 449C) at a heating rate of 10 °C min⁻¹ in air. The crystal structures of the cathode materials prepared by the three methods were analyzed by X-ray

diffraction (XRD, Bruker D8), and the particle morphology of the NCM powders was characterized by scanning electron microscopy (SEM, Supra55VP, Zeiss).

2.3 Cell assembly and electrochemical tests

The cell assembly of NCM cathode material has been described in detail in our previous article [9]. Charged/discharged tests were performed on a multichannel battery testing system (BTS-51, Neware, China) with voltage ranges between 2.5 and 4.5 V and current densities between 0.2 and 5 C rates (1 C = 200 mAh g⁻¹). Cyclic voltammograms (CVs) were measured on an electrochemical workstation (CHI650, Chenhua, China) with a scan rate of 0.1 mV s⁻¹.



3. RESULTS AND DISCUSSION

Figure 1. The TG-DSC curves of NCM precursor powders synthesized by different methods. The test temperature ranges from 40 °C to 1000 °C with the heating rate of 10 °C min⁻¹.

In order to determine the reaction temperatures required for the three preparation processes, thermogravimetric analysis was performed on the precursor samples, and the TG-DSC curves are shown in Fig. 1. From the figure, it can be seen that there are two stages of weight loss in S1 and S2 precursor powders, and three stages of weight loss in S3. The first stage in S1 that occurs below 200 °C is mainly

the decomposition of crystal water and acetate in the raw material, and the reaction is exothermic. And the endothermic weight loss reaction occurs between 302 °C and 378 °C, which is the stage of NCM crystal formation. Similarly, the small weight loss of the S3 precursor below 200 °C is the removal of crystal water from the raw materials. The second stage of weight loss below 300 °C is the decomposition process of oxalate, and the third stage is the main reaction with temperatures between 300 °C and 310 °C. The S2 precursor is dried and contains an organic polymer that decomposes in the first stage and reacts in the second stage at temperatures ranging from 314 °C to 355 °C. It can be seen that the reaction temperatures of the precursors of the three preparation methods are similar.



Figure 2. XRD patterns of NCM powders synthesized by different methods. The diffractometer uses Cu K α radiation source ($\lambda = 1.54178$ Å) in the 2θ range of 15-70° at a scan rate of 5° min⁻¹.

The XRD patterns of NCM powders synthesized by the three methods are shown in Fig. 3. The main diffraction peaks are labeled with *hkl* indices. All diffraction peaks of the three samples can be assigned to the hexagonal α -NaFeO₂ structure with the space group of *R-3m*, and no diffraction peaks of impurity phases are observed. The obvious splitting of (006)/(102) and (018)/(110) peaks indicates that the NCM powders have a highly ordered layered structure. [12, 13]. As mentioned before, cation mixing between Ni²⁺ and Li⁺ often occurs during the preparation of NCM materials. In such ternary materials, the intensity ratio of the (003) and (104) diffraction peaks is considered as an indicator of cation mixing between Li⁺ (3a site) and transition metal (TM) ions (3b site) [2]. When I₍₀₀₃₎/I₍₁₀₄₎ is greater than 1.2, it means less cation mixing between Li⁺ at the 3a site and TM ions at the 3b site in the crystal. The intensity ratios of the (003) and (104) peaks and the lattice parameters of the samples are shown in Table 1. Compared with the cathode materials with only one TM element such as LiCoO₂ and LiMn₂O₄, NCM materials

combine three TM elements, among which Ni^{2+} is difficult to oxidize to Ni^{3+} , and Mn ions also exist in 2, 3, 3.5 and 4 valence states, which makes the reaction process more complicated and therefore more likely to affect the structural stability of the materials. The results of this work suggested that the samples prepared by co-precipitation method had the lowest degree of undesirable cation mixing among the three samples.

Synthesis method	a (Å)	c (Å)	$I_{(003)}/I_{(104)}$
Solid-state (S1)	2.868	14.276	1.20
Pechini (S2)	2.861	14.228	1.21
Co-precipitation (S3)	2.859	14.226	1.43



Figure 3. SEM images of NCM powders synthesized by different methods. The three samples differed significantly in morphology.

Fig. 3 shows the SEM images of the NCM powders prepared by different methods. There are obvious differences in the morphology of the three samples. The S1 sample has two morphological distributions, small particles (200-400 nm) and larger ones (600-800 nm), and the particles are all rock-

like with sharp edges. The NCM particles of S2 are loosely agglomerated and more uniformly distributed, with a particle size of about 200-500 nm. The disk-shaped NCM particles are found in the S3 sample, and the average size of the particles is the largest among these three samples, ranging from 300 to 700 nm. In this method, when the lithium source and pre-calcined precursors are mixed and calcined in a furnace, small particles are agglomerated into large micro-sized particles by continuous calcination [15]. It is well known that the particle shape and size of cathode materials affect the energy density in practical applications, so it is important to control the particle morphology [6].



Figure 4. Initial charge/discharge curves of NCM cathode materials synthesized by different methods at 0.2 C rate with voltage range from 2.5 V to 4.5 V.

The first charge/discharge curves of NCM electrodes prepared by different methods at 0.2 C rate are shown in Fig. 4. The shapes of the first charge/discharge curves of the NCM electrodes synthesized by different methods are basically the same, but the specific capacities are different. The initial discharge capacities of the S1, S2, and S3 samples are 154.6 mAh g^{-1} , 183.3 mAh g^{-1} and 176.8 mAh g^{-1} , respectively. The first discharge capacity of the S1 sample is only 84.3% of that of the S2 sample, but there is no significant difference in the first charge/discharge coulombic efficiencies of the three samples, which are 82.1 %, 82.9 % and 82.5 %, respectively. This may be due to the smaller and homogeneous NCM particles prepared by the Pechini method, which contributes to the accessibility of the redox centers, resulting in a lower total polarization and making the reversible capacity larger [16]. In addition, the large charge/discharge plateau difference of the S1 sample also proves the presence of large electrode polarization, which leads to poor reversibility of lithium ions during the insertion and desertion, and therefore the capacity is weakened [5]. Shi et al. reported the first synthesis of NCM cathode materials using flash/field-assisted sintering technique [17]. The FS-1.2A sample showed the best initial discharge

capacity of 179.7 mAh g⁻¹, which the author attributed to its better layered crystal structure and a relatively smaller average particle size.



Figure 5. Cycling performances of NCM cathode materials synthesized by different methods at 0.2 C and 1 C rates. Each sample is cycled 50 times consecutively.

The cycling performances of NCM cathode materials prepared by different synthesis methods at 0.2 C and 1 C rates are shown in Fig. 5. After 50 charge/discharge cycles, the discharge capacity of all three samples decreased. Both S1 and S3 samples show one or two cycles of activation during the cycling process, while there is no significant decrease in the discharge capacity of the S2 sample in the first cycle. At the rate of 0.2 C, the discharge capacity of the S2 sample is similar to that of the S3 sample. The maximum discharge capacity of the S3 sample at 0.2 C is 177.0 mAh g⁻¹ with a capacity retention rate of 77.9% after 50 cycles, while the capacity retention rate of the S2 sample is slightly higher than that of the S2 sample, reaching 165.9 mAh g⁻¹, with the capacity retention rate of 75.4 % after 50 cycles, which is also slightly higher than that of the S2 sample at 73.1%. After 50 cycles at 0.2 C and 1 C, the capacity retention rates of the S1 sample are only 60.8% and 61.8%, respectively.

Comparing the three samples synthesized by different methods, the sample prepared by the coprecipitation method has the best cycling performance. This result is consistent with the XRD result, where the S3 sample has the highest $I_{(003)}/I_{(104)}$ value of 1.43. The high discharge capacity and stable cycling performance of NCM can be attributed to its highly ordered layered structure and less cation mixing, which can endure the deintercalation/intercalation process of lithium ions and maintain a stable crystal structure [6]. On the other hand, the large crystalline grains of S3 sample reduce the contact area with the electrolyte, avoiding the deterioration of the electrode/electrolyte interface and facilitating the reversible deintercalation/intercalation of lithium ion [18]. In the flash/field-assisted sintered samples synthesized by Shi et al., the FS-1.2A sample showed a higher capacity retention rate of 83.4% after 50 cycles at 64 mA g⁻¹ [17]. The authors speculated that the increase in capacity retention may be due to the increased ionic conductivity caused by electric field-assisted sintering.



Figure 6. Discharge capabilities of NCM cathode materials synthesized by different methods at various current rates from 0.2 C to 5 C.

The rate capabilities of the three samples are assessed after 5 charge/discharge cycles and the results are shown in Fig. 6. At low discharge rates below 2 C, the S2 and S3 samples can deliver most of the reversible capacity and they are very close. However, at higher rate of 5 C, remarkable differences in the discharge capacities are observed for these two samples. The minimum discharge capacities of the S3 and S2 samples at 5 C are 115.5 mAh g⁻¹ and 105.0 mAh g⁻¹, respectively. Compared to these two samples, the S1 sample has the lowest discharge capacity at the entire discharge rates. The discharge capacities of the co-precipitated sample reached 184.1, 169.2, 157.0, 142.8 and 116.7 mAh g⁻¹ at the rates of 0.2, 0.5, 1, 2 and 5 C, respectively, while the discharge capacities of the S1 sample are 156.9, 142.3, 127.1, 104.2 and 75.0 mAh g⁻¹, respectively. At a high rate of 5 C, the discharge capacities of S1, S2 and S3 samples are 47.8 %, 62.9 % and 63.4 % of those at 0.2 C rate, respectively. The best rate performance of the S3 sample is considered to be related to its well-defined layered structure and better cation ordering [19]. It is known that the rate capability of cathode material depends heavily on the electrochemically active surface area and the diffusion distance of lithium ions [20]. Although the $I_{(003)}/I_{(104)}$ value of the S2 sample is relatively low, its uniform and fine particles can effectively increase the specific surface area of the active material, which is conducive to the diffusion of lithium ions [9]. For the S1 sample, it is believed that the enhancement of the electrode polarization at high rate leads to the deterioration of rate performance.



Figure 7. The CV curves of NCM cathode materials synthesized by different methods. The scan rate is 0.1 mV s^{-1} .

Fig. 7 shows the CV curves of the NCM electrodes synthesized by different methods. All three samples have obvious redox peaks, which are consistent with the previous article that the redox peaks originating from the redox of Ni²⁺/Ni⁴⁺ couples at around 3.6-4.2 V [21]. In general, the potential interval value (ΔV) of the redox peaks reflects the strength of the electrode polarization, and the larger the potential interval value, the stronger the electrode polarization [22]. For S1, S2 and S3 samples, the oxidation/reduction peaks appeared at 4.14/3.63, 4.01/3.68 and 3.90/3.68 V vs. Li/Li⁺, corresponding to the ΔV of 0.51, 0.33 and 0.22 V, respectively. The smallest ΔV is observed for S3 sample, indicating that it has the smallest electrode polarization and the best reversibility. In addition, the relationship between the redox peak current i_p and the diffusion coefficient D_{Li} of lithium ions in the electrode can be expressed as follows [23]:

$$i_p = 2.69 \times 10^5 n^{3/2} A D_{Li}^{1/2} c v^{1/2}$$
 (1)

where ip is the peak current (A), n is the number of electrons per species reaction, A is the electrode area (cm²), D_{Li} is the diffusion coefficient of lithium ions (cm² s⁻¹), c is the concentration of lithium ions in the cathode (mol cm⁻³), and v is the potential scan rate (V s⁻¹). With the same electrode preparation and testing procedure, it can be assumed that the diffusion coefficient D_{Li} is proportional to the square of the peak current i_p . From the CV curves, the peak current i_p is the largest for S3, implying that this electrode has the largest lithium ions diffusion coefficient D_{Li} . This can also explain that the NCM cathode material synthesized by co-precipitation method has the best rate performance by reducing the diffusion resistance of lithium ions.

4. CONCLUSIONS

In summary, the NCM cathode materials were synthesized through the solid-state, Pechini and co-precipitation methods, and their structures, morphologies, and electrochemical properties were compared. The sample prepared by the co-precipitation method has a highly ordered layered structure, low cation mixing and large particle size, which can effectively reduce the electrode polarization and enhance the reversibility of lithium ions. As a result, it has excellent cycling stability and rate performance compared to those synthesized by the other two methods. These results imply that through continuous research, improved synthesis methods for NCM cathode materials can be found to meet the higher requirements for the development of the LIB industry.

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