

The Synthesis and Electrochemical Properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ Cathode Materials by a Co-precipitation Method

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Abstract. The layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material was synthesized Using carbonate co-precipitation. During the preparation of precursors, the reaction conditions have great influence on the morphology, dispersion, uniformity of precursors, and therefore affect the electrochemical properties of cathode materials. This paper focused on the different feed rate of Na_2CO_3 solution has produced experimental results. SEM test shows when the feed rate of Na_2CO_3 solution is 0.5 ml/min, the synthesized material is spherical morphology, good size distribution and crystallinity. Energy spectrum describes Ni, Co, Mn elements of precursor close to the theoretical value. The XRD shows $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material for $\alpha\text{-NaFeO}_2$ layered structure. Electrochemical test curve shows at the appropriate feed rate the discharge capacity is up to 177mAh/g. After 50 cycles, the capacity retention rate was 80.5 percent. The cyclic voltammetry curves have proved good electrochemical performance of the cathode materials. The impedance spectrum curves have showed the low of resistance Rct.

Introduction

Layered LiCoO_2 cathode materials have obtained large-scale commercial applications, but the element of Co is toxic, higher cost and the LiCoO_2 possess low hematocrit, poor safety performance. Therefore its development has been limited further [1]. Lithium-ion batteries have currently become demands for portable electronic devices and electric vehicles because of their higher output voltage and high energy density than other rechargeable systems [2, 3]. In 1999, Liu proposed composite cathode material of Li-Ni-Co-Mn-O ternary layered structure for lithium-ion battery. Due to the synergistic effect of nickel, cobalt and manganese, the Li-Ni-Co-Mn-O composite cathode material have favorable electrochemical performance than any single component, and combines the advantages of three components, which makes up for their shortcomings, more than high-capacity, low-cost, long cycling performance and safety performance characteristics [4-6], considered to be one of the alternative LiCoO_2 cathode material. Because of the Ni, Co, Mn three elements ratio of 1: 1: 1 in the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material, the advantages of the three elements can be integrated, and become a focus of research about lithium-ion battery materials.

This article was prepared $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material by used carbonate co-precipitation. The carbonate of nickel, cobalt and manganese are stable and insoluble, and the solubility product are similar, which is relatively easy to obtain the product fulfilling atomic level mixing [7]. In this study, in order to obtain $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{CO}_3$ precursor, carbonate need be made precipitate [8-10], and controlled crystallization co-precipitation. After heat treatment, the oxidation of nickel, cobalt and manganese was synthesized. In the previous literature, the course of the reaction need be control by adding aqueous ammonia as complexing agent, without considering the effects of Na_2CO_3 in the experiment. In this experiment, the feed rate of Na_2CO_3 solution be adjusted to analyze the morphology and properties of precursor and cathode materials.

Experimental

The reagent-grade $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were used to prepare $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. Firstly, Metallic acetates were dissolved in distilled water to dub sulfate salt solution as 1 mol L^{-1} (solution 1). The aqueous ammonia was used as precipitant and was dissolved into solution of 1 mol L^{-1} (solution 2). Meanwhile, Na_2CO_3 was used as a solution of 1 mol L^{-1} . The solution 1 and solution 2 are simultaneously fed into a stirred reactor. During the reaction, the Na_2CO_3 solution was added by different feed rate for 0.3, 0.5, 1, 1.5 ml / min, with the stirring speed at 1200 rpm. The co-precipitate was aged 6 hours at temperature of 50°C and then we can obtain the morphologies of $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{CO}_3$ precursor particles. The precursor was washed using distilled water for sulfate and sodium ions and was dried at 120°C for 12 hours. After the precursor was heated at 700°C for 3 hours, the precursor oxide $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ uniformly was mixed with $\text{LiOH} \cdot \text{H}_2\text{O}$. The mixtures was calcined at 550°C for 5 hours, and then calcined at 900°C for 12 hours to facilitate the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material, cooled to room temperature with the furnace. The cathode material was labeled as a, b, c, d.

The microstructure for as-synthesized precursor was observed by Japanese company Hitachi S-4500 SEM type. The chemical element Ni, Co, Mn content of precursor was analyzed by EDS. The crystal structure for as-synthesized cathode materials were characterized by X-ray diffraction (XRD, D/max 2200/PC, Rigaku, 40kV, 20mA, Cu $K\alpha$ radiation, $\lambda=1.5406 \text{ \AA}$). XRD test results were analyzed with MDI Jade6.5.

For the electrochemical measurements, the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials were mixed with 15 wt% carbon black and 5wt% polytetrafluoroethylene binder. This mixture was coated on an aluminum mesh and dried under vacuum at 120°C for 8 hours. After the mixtures was cut into the cathode pieces, we need weighed the cathode sheet accurately and calculated the quality of active materials. Using the lithium as anode pieces and 1 mol L^{-1} of LiPF_6 dissolved in ethylene carbonate vinegar (EC)/dimethyl carbonate (DMC)/ethylmethyl carbonate (DEC) (1: 1: 1) as the electrolyte, the cathode pieces was assembled into CR2032 button cell battery in a glove box. The button cell battery was tested for the electrochemical performance on ArBin between the 2.5 and 4.6V.

Results and discussion

During the process of co-precipitation reaction, the selection of feed rate is a key factor affecting the particle morphology and performance. It has a great influence on crystal morphology, dispersity, particle size. For obtaining spherical crystal structure, we should choose the best feed rate. Fig. 1 shows SEM images of a carbonate precursor prepared at different feed rate of Na_2CO_3 solution. The SEM images indicate that the particle size is uniform, dispersed and spherical in fig. 1(b). Moreover, it is compactness, good dispersion, no trend to reunion and about 5 μm . The good dispersion of particle is conducive to the active substance in contact with the electrolyte and ensure that the chemical properties of the cathode material. The reason is because in the high-speed stirring solution, the appropriate feed rate is favor to nucleation and growth of grains, and higher or lower feed rate is difficult to form spherical particles with good dispersibility.

The content of nickel, cobalt, manganese at the feed rate of 0.5 ml/min was determined by EDS elemental analysis. The results are shown in fig. 2. The theoretical content ratio of Ni, Co, Mn in $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{CO}_3$ is 1: 1: 1, and the synthesized material is 1.03: 1: 0.94 actually. By this we learn that the ratio of Ni, Co and Mn in the synthesized $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{CO}_3$ precursor is close to theoretical values.

Fig. 3 shows XRD patterns for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials (a, b, c, d). As can be seen from the XRD patterns, four samples have a standard α - NaFeO_2 layered structure [11], consistent with the reported [12-13]. The figure shows that space group of the materials is R-3m. No miscellaneous indicate peak that no other materials were found, and the calcined materials is good crystallinity. The splitting peaks (006)/(102) and (108)/(110) is clear, but the splitting peak

(006)/(102) of a sample is more obvious than b, c, d sample. This indicates that in the case of lower feed rate it is difficult to form a good layered structure, and suitable feed rate is easy to form preferred layered structure. In $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials, shuffle is prone and will affect the performance of the material because of Li^+ (0.076nm) and Ni^+ (0.069nm) radius value very close. In earlier report, the I(003)/I(104) ratio is used to judge the degree of shuffling cations. When I(003)/I(104) ratio is smaller, the greater the degree of shuffling. In XRD patterns, the feed rate of 0.5 ml/min, degree of shuffling is small.

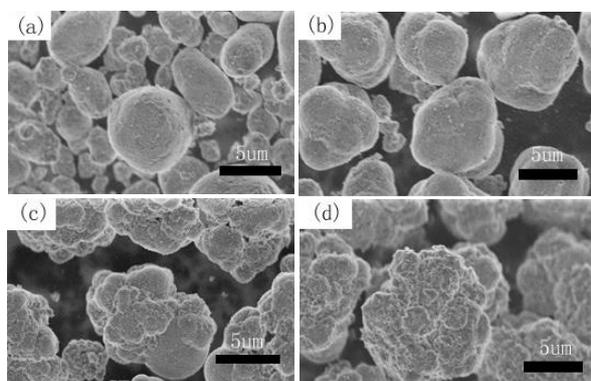


Fig. 1 The SEM pictures for precursor at different feed rate of Na_2CO_3 solution: (a)0.3 ml/min,(b)0.5 ml/min,(c)1.0 ml/min and (d)1.5 ml/min

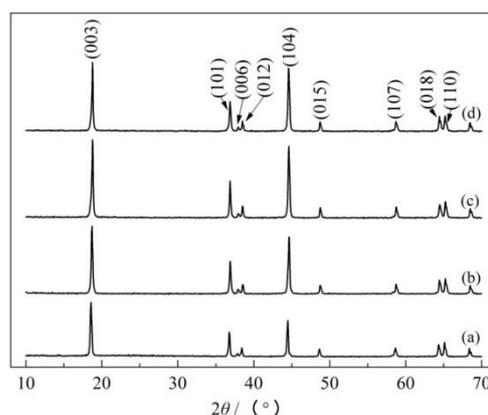


Fig. 3 The XRD patterns for cathode materials: (a)0.3 ml/min, (b)0.5 ml/min,(c)1.0 ml/min and (d)1.5 ml/min

Fig. 4 shows cycle characteristics for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials (a, b, c, d). The four samples of a, b, c, d are tested at 0.1C discharge rate, and the first discharge were 176,177,173 and 170 mAh/g, respectively. After 50 cycles, the capacity retention rate is 69%, 80.5%, 70% and 73%, separately. This indicates that the cycle performance of the cathode material can be affected by the Na_2CO_3 solution feed rate. Within an appropriate range, the cycle performance will increase with the rise of the Na_2CO_3 solution feed rate. When the feed rate is 0.5 ml / min, the cycling performance is best.

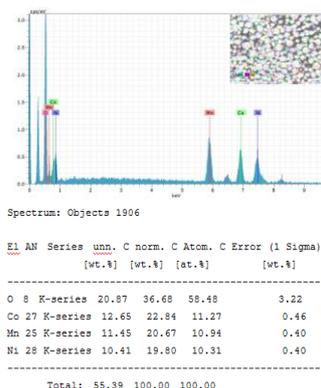


Fig. 2 The EDS picture for precursor at the feed rate of 0.5 ml/min

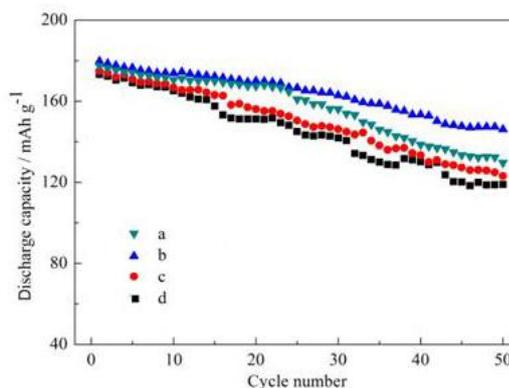


Fig. 4 The cycle characteristics for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials: (a)0.3 ml/min, (b)0.5 ml/min, (c)1.0 ml/min and (d)1.5 ml/min

Fig. 5 shows the cyclic voltammetry (CV) test for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials (a, b, c, d) in the charge and discharge process. Fig 5.a-d show the electrochemical reaction for four samples during the first three cycles. Since the voltage range does not exceed 2.5-4.6V, Mn^{4+} is not active

and the charge / discharge reaction are corresponding to the Ni²⁺/Ni⁴⁺ and Co³⁺/Co⁴⁺ redox. The figures show that the voltage is 3.97V at main oxidation peak, while the voltage 3.53 V at reduction peak, corresponding exactly to the Ni²⁺/Ni⁴⁺ redox process. A unique redox zones between 3.97V and 3.53V are observed, consistent with previous studies, which indicate that the redox process does not change structure, especially from hexagonal to monoclinic phase. So, the desired cathode materials with good charge/discharge reversibility are synthesized. Compared figure (b) with (a), (c) and (d), the disparity of first cycle and continuous cycle of redox peaks is small between 2.5 and 4.6V. Moreover the (b) is good reproducibility and possess the best electrochemical properties.

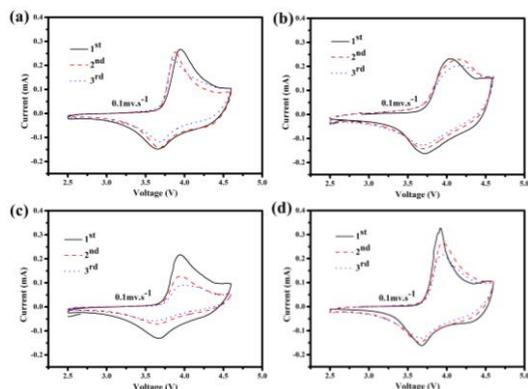


Fig. 5 The cyclic voltammetry (CV) test for cathode materials: (a)0.3ml/min, (b)0.5 ml/min, (c)1.0 ml/min and (d)1.5 ml/min

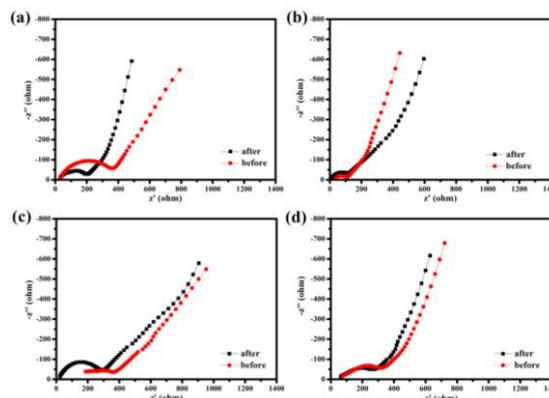


Fig. 6 The EIS curve for cathode materials: (a) 0.3 ml/min, (b)0.5 ml/min, (c)1.0 ml/min and (d)1.5 ml/min

Fig. 6 shows the impedance spectrum measured curve (Z'' and Z') for LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode materials (a, b, c, d) in the open state. EIS curve [14-15] consists of two areas, which one in the high frequency semicircle area and other slash (Warburg-type element) is located in a low frequency. The semi-circular of high frequency range is shown as the resistance R_{ct} of a charge transfer in the EIS curve. In the low frequency region, the Warburg resistance Z_w is corresponding to a large number of lithium-ion diffusion in electrode, which has been used to determine the diffusion coefficient of lithium-ions in the positive electrode material. After 50 cycles, the resistance R_{ct} of a, b, c and d have different rate of increase, with 40%, 26%, 53% and 45%, respectively. The results show that the potential of the sample b after circulation is the lowest, having a good cycle retention rate, which is consistent with the results in discharge cycle of fig. 4.

Conclusion

Layered LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode materials were synthesized by carbonate co-precipitation method. In the process of preparation, the feed rate of Na₂CO₃ solution was adjusted to study its influence on the morphology of the synthesized Ni_{1/3}Co_{1/3}Mn_{1/3}CO₃ precursor. When the feed rate of Na₂CO₃ solution is 0.5 ml/min, the particles are spherical, uniform distribution. The actual value of Ni, Co, Mn elements are close to the theoretical value. The calcined oxide is a standard α -NaFeO₂ layered structure in the picture of XRD. The Electrochemical performance shows that the discharge capacity of the synthesized LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode material at suitable feed rate of Na₂CO₃ solution can reach 177mAh/g. After 50 cycles, the discharge capacity retention rate is 80.5%, with good cycle performance. CV and EIS curves also have proved good performance of the cathode materials.

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