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Short Communication

Synthesis of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ Cathode Material in Acetate System for Lithium-Ion Battery

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This paper adopted the co-precipitation method with acetate as raw material to prepare $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]$ O_2 in acetic acid system, which was analyzed by XRD, SEM and electrochemical testing methods, studying the performance of the cathode material under different calcining temperature and calcine time. The results showed that the optimum calcines temperature and time of the sample were respectively 800℃and 8h; under the optimal calcine temperature and time, the first charge and discharge capacity was 161.788mAh/g and the discharge specific capacity was 92.242mAh/g at 0.1 C rate; after the 20 times cycle test, the charge and discharge efficiency of materials can be over 95%.

Keywords: Lithium-ion battery; Acetate system; Anode material; Calcine temperature; Calcine time

1. INTRODUCTION

Lithium-ion battery, a new generation of secondary battery, is one of the emphasis on the research of chemical power source. It has the advantages of high energy density, long cycle life, good safety performance, environmental protection and other advantages [1-3]. which is commonly used in power electronic devices and electric vehicles. The powers supply has been widely used in household appliances, and also begins to apply to the field of aviation, aerospace, marine and other field. $LiCoO_2$ as cathode materials for lithium-ion batteries is now widely used in the market, but cobalt is a high price and scarce material, which is toxic and is the pollution of the environment. The spinal $LiMn_2O_4$ can overcome some shortcomings of $LiCoO_2$, however, the cycle performance of this material capacity are relatively poor, the application is limited; $LiFePO_4$ has the advantage of reducing the cost, good performance, and is an ideal material to except the poor conductive property and low specific capacity. Therefore, the development and application of lithium-ion batteries should be equipped with not only a high capacity, good performance and low cost, but also the exploration of non pollution, which is the future direction of development.

$LiNi_xCo_yMn_zO_2$, a multiple material, is of good safety performance and low cost , combining the advantages of single $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$, through the synergistic effect between Ni, Co and Mn forming the transition metal embedded lithium oxide, a new type of composite cathode material [4]. The rich lithium manganese base shaped cathode material $xLi_2MnO_3\cdot(1-x)$ $LiMO_2$ (M=Ni, Co, Mn, $0 \leq x \leq 1$) is newly discovered, comparing with other common materials, it has the edge of lower cost, better safety performance and less pollution, which is a new generation of cathode materials for lithium-ion batteries and is paid great attention by domestic and foreign scholars [5-6].

Similar to single element cathode material, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is the α-$NaFeO_2$ type layered structure material, which belongs to the hexagonal, space group R3m [7]. The three element materials also have disadvantages, the main problem is the synthetic difficulties, the synthesis process is more complex, its charge and discharge cycle reaction cannot be tested under the condition of high rate, the cycle performance of the battery will be severely affected by excessive voltage, charge and discharge performance and cyclic performance will be worse. These defects influence the performance of cathode materials and also limit the scope and space of this kind of materials, so its limitations of development still exists [8].

Used a feasible solution process in ternary system to synthesize the novel $Li_2Fe_{1/3}Mn_{1/3}Ni_{1/3}SiO_4/C$ by Rong Yang [9], the experience shows an initial discharge capacity of 181.4 mAh/g and a discharge capacity of 172.9 mAh/g after 20 cycles at 0.1C in the voltage range of 1.5–4.6V. Zhang [10] present a Silkworm-like spherical Ni-rich Layered $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode materials were assembled with uniform nanoparticles , the experimental results show that the discharge specific capacity of this method of the synthesis of cathode material are 201.1 and 142.5 mAh/g, respectively, when cycled at 0.1 and 5C. After 115 cycles the electrode still maintains a capacity of 138.2 mAh/g. Liu [11] prepared material by a facile and efficient synthetic method, after testing it can be found that the initial discharge of the material reaches 213.9 and 121.6 mAh/g at 0.1 and 10C, respectively, whereas the pristine electrode only shows 196.8 and 92.1 mAh/g. Zheng[12] synthesizes $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ by the method of co-precipitation followed by solid-state,The tests demonstrate The fresh-synthesized and the re-synthesized sample delivered discharge capacities of 150.3 and 148.8 mAh/g at 1st cycle. Huang [13] used co-precipitation method to synthesize $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ precursor and calcined, charge and discharge tests at rates of 0.1C and 1C, the first discharge capacity is 199mAh/g and 170mAh/g, respectively. After 80 cycles at 1C the discharge capacity retention was 92%.

$Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ belongs to one of the rich lithium manganese base series materials of $xLi_2MnO_3\cdot(1-x)LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (x=0.5), which is the current research hot-spot. This thesis mainly adopts co-precipitation preparing the manganese base shape lithium rich material $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ of acetic acid system , using XRD、SEM and electrochemical test measure to characterize the process parameters of the calcine temperature and calcine time. From that we can determine the optimum synthesis process so as to obtain the excellent performance of the layered rich lithium cathode material.

2. EXPERIMENT

2.1 Preparation and characterizations of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$

First, in brief, the required quality of three kinds of salt Ni, Co, Mn raw materials were took into the beaker dissolved by distilled water, then the transition metal salt was dissolved fully by used magnetic stirrers,which formed 1 mol/L solution of transition metal ions; then the prepared 2 mol/L NaOH solution as precipitant was added into the solution drop-wise, keeping the solution stirring for a period of time to ensure the transition metal solution in complete precipitation until the color of the mixed suspension staying unchanged after dropping; the fully mixed slurry was filtered by filter pump and then was washed several times to make the precipitation out of remained ions; the dried precipitation was finely powdered in an agate mortar with proper amount of alcohol, then the prepared precursor was done in this way again with a certain mount of $LiOH·H_2O$ to get the mixed powder, after which the mixture was Calcined at a certain temperature for some time, was removed after natural cooling and then was finely powdered ,getting the anode material $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$. The experimental procedure of the anode material prepared by co-precipitation are shown in Fig. 1.

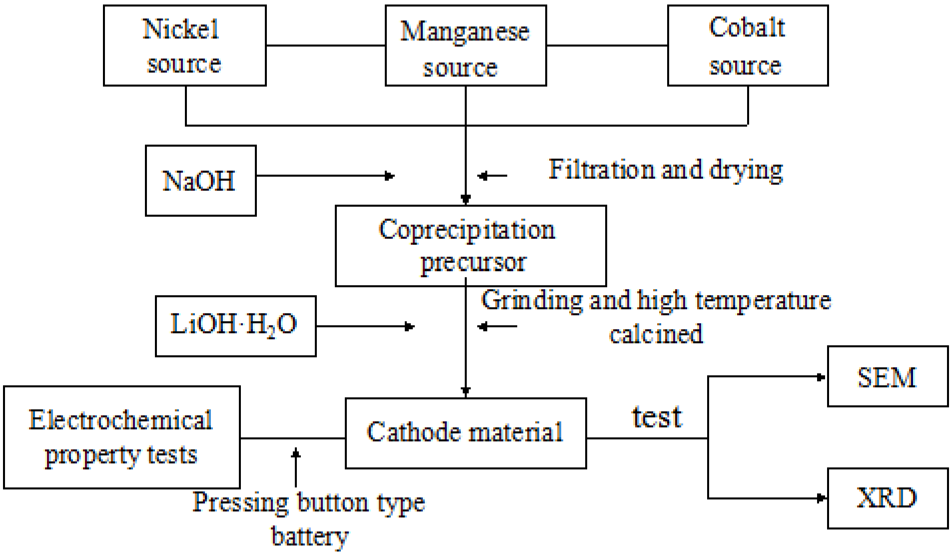

Figure 1. Preparation process flow diagram of co-precipitation method

2.2 Characterizations of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$

The as-synthesized anode material was characterized by XRD and SEM. The phase purity and crystal structure of powders were identified by a powder X-ray diffraction (XRD, 2250V, Rigaku) using Cu-Kα radiation (λ=0.15418nm) in the 2θ range of 10-80, scan rate of 5°/min, working voltage of 35kV and working current of 30mA. SEM (S-4800N, Japan) was employed to analyze the micro-morphology.

2.3 Electrochemical measurements

The text sample used for electrochemical performance was prepared by two- electrode button-battery, which was based on 82032 type button cell of Li[$Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}$]$O_2$/$LiPF_6$ (EC:EMC:DMC¼1:1:1 in volume)/Li. The anode electrode was made of 80 wt.% , Li[$Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}$]$O_2$ powder as the active material, 10 wt.% carbon black as conducting agent, and 10 wt.% polyvinlylidene difluoride(PVDF) as binder dissolving in N-methylpyrolidone (NMP). After being blended in NMP, the mixture was spread uniformly on aluminum foil current collector and dried in vacuum for12h at 120 ℃. The metallic lithium foil and a polypropylene micro-porous film were used as the cathode and the separator respectively. The assembly of the cells was carried out in a controlled environment using a glove box under a dried argon atmosphere. The cells' discharge/charge tests were carried out over a voltage range of 2.0-4.6V vs. Li/Li^+ with 0.1C rate on a BTS-5V multi-channel workstation manufactured by Shenzhen Xinweier, China. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of the cells were measured on an electrochemical workstation (CHI660D, Shanghai Chenhua, China). The scan rates and the potential range of the CV were 0.1 mV/s and 2.0-4.6V respectively, and the frequencies of the EIS ranged from 100 kHz to 0.01 Hz. All the electrochemical measurements were conducted at room temperature.

3. RESULTS AND DISCUSSION

3.1 The effects of calcine temperature

Different calcine temperature has a great influence on the properties of synthetic materials. If the temperature is too low, the reaction is not complete, then resulting no target product produced, in turn, if high temperature, generated structure and performance of the material would be worse. This paper studied different calcine temperature, the calcine precursor mixture was respectively carried on at 700℃, 750℃, 800℃, 850 ℃, 900℃ to optimize the calcine temperature. Fig. 2 shows comparison diagram of XRD for cathode material of acetic acid system in different calcine temperature conditions. There is no obvious difference of XRD spectra of samples with different calcine temperatures in acetic acid. Diffraction curve in the figure is more uniform and artifactual bands are not obvious, which indicates that the sample is pure phase crystal structure material. Between 20 to 25 degrees, there are the characteristic peaks in all material of Li_2MnO_3 in the diffractograms , the diffraction peaks could be diffraction peak of $LiMn_6$ superlattice, which proved that the monoclinic crystal structure of cathode materials. Through the comparison with the standard atlas, additional diffraction peaks could match the standard spectral graph completely, suggesting that they belonged to α-$NaFeO_2$ layered structure materials and had a good crystal structure.

The morphology of each material in the graph XRD intuitively and clearly shows that with the increasing of the calcine temperature, the diffraction peak intensity becomes stronger, the peak width begins to narrow, calcine temperature of 800 ℃ sample diffraction peak intensity and width is much better than calcine temperature of 700℃ and 750 ℃. With the increasing of calcine temperature, the intensity of the diffracton peak begins to weaken, the diffraction peak intensity of 850 degrees of Calcined sample comes to weaken, the main diffraction peak width becomes larger, the Li_2MnO_3 characteristic peak almost disappeared, suggesting that the crystalinity of the samples began to change, and the calcine temperature of 900 ℃ samples, between 35~40 degrees, it appears a smaller of the diffraction peaks, it shows that the material itself may be the formation of a new phase, of which the intensity of the diffraction peak is weaker than 800 ℃. Above all, it concludes that, with the increase of the calcine temperature, the diffraction intensity peaks are from low to high, then from high to low, the diffraction peak intensity of the strongest peak is narrow, the most prominent characteristic peaks appears at 800 ℃, Therefore, the optimal calcine temperature is chosen as 800 ℃.

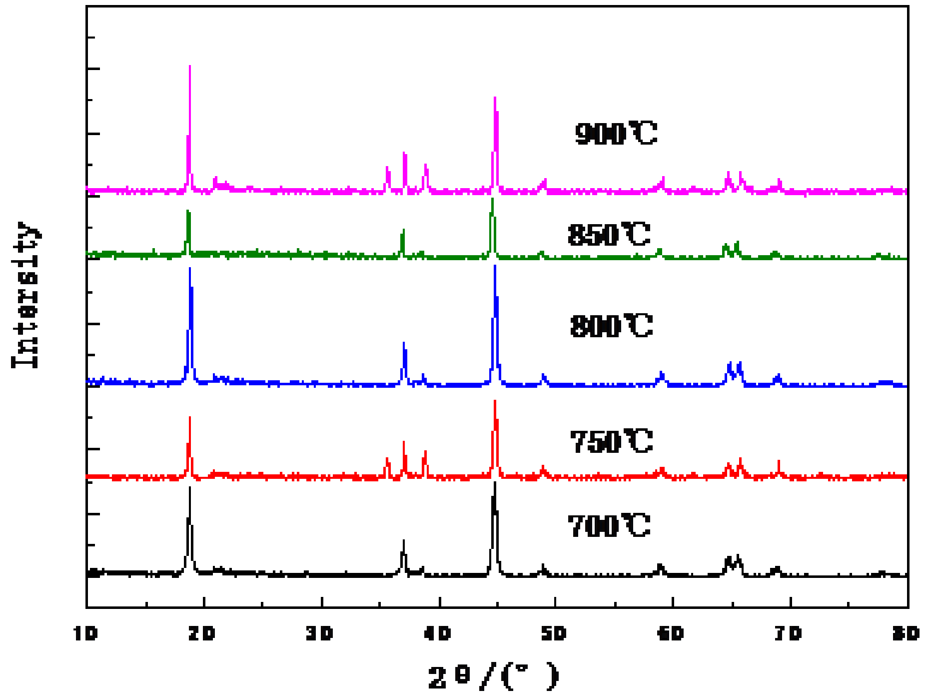

Figure 2. XRD patterns of samples prepared at different temperatures of calcine time for 8h

Fig. 3 shows SEM diagram in 10.0K magnification of the different calcine temperature of cathode material, its layered structure starts generating at 700 ℃, particle size is uniform and surface is smooth; layer structure of sample at 750 ℃begins to be clear and the particle size begins to increase; the micro morphology of samples at 800℃is best, at which sheet structure is clear, ordered, the accumulation of particles have administrative levels feeling and the surface is smooth, no agglomeration is on it, crystallinity of the material is the best; it begins to appear agglomeration at 850℃, material begins to appear adhesion, forms the bulk of large particles, of which the crystallinity comes to decrease; the reunion phenomenon continues to increase at 900℃, in diagram are presented massive particles and no Layered structure exits, so the crystallinity is worse.

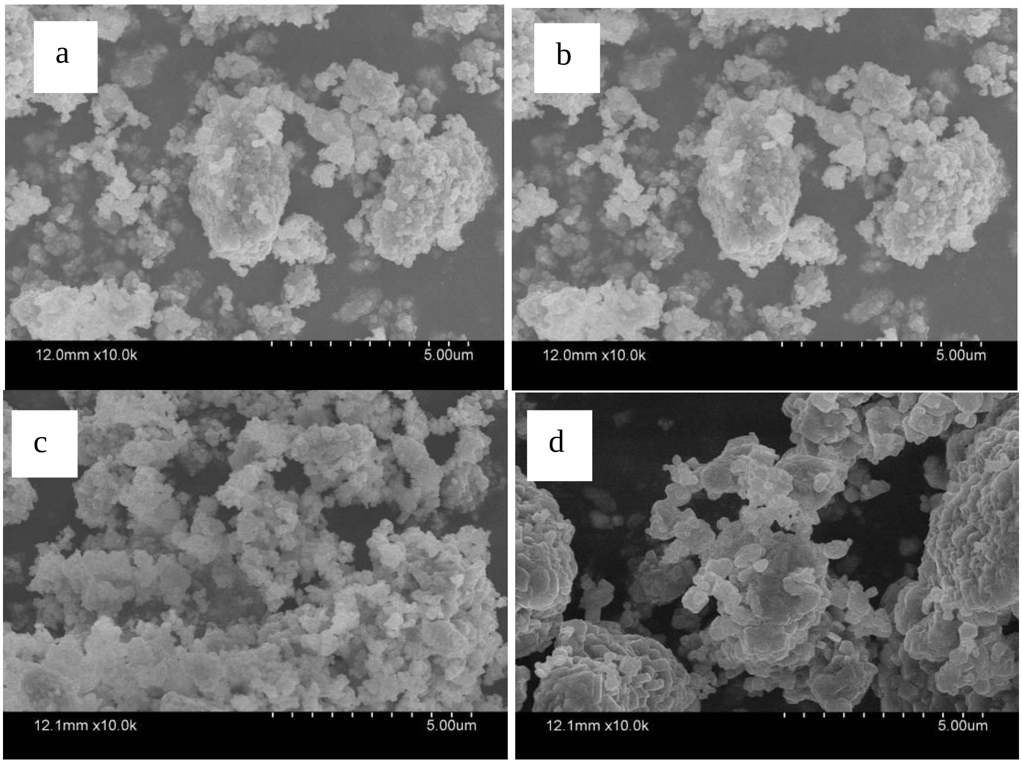

Figure 3. The SEM graphs of samples prepared at different temperatures (a=700℃; b=750℃; c=800℃; d=850℃)

3.2 The effects of calcine time

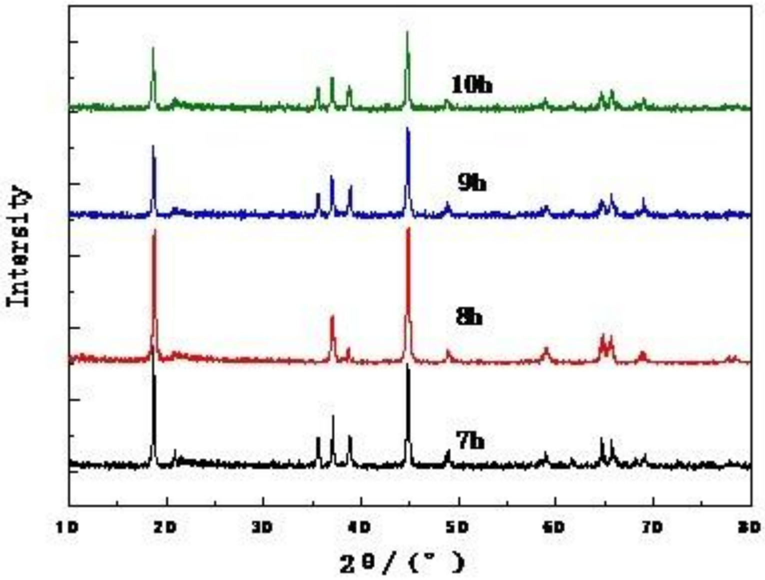

Figure 4. XRD patterns of samples prepared at different time of calcine temperature for 800℃

Fig. 4 shows XRD spectra of prepared cathode material that calcine time respectively as 7h, 8h, 9h and 10h. It can be directly seen from the chart that the shape and position of XRD diffraction peaks of different time of calcine specimens generally are consistent, the characteristic peak is obvious and no impurity peaks exits, between 20 to 25 degrees the characteristic diffraction peaks of Li_2MnO_3 appears and characteristic peak intensity has little difference. At 65 degrees two peaks obviously splits. Comparing with the standard card, it shows that they are layered material with α-$NaFeO_2$, which indicates firing obtained samples have good crystalline structure at the same temperature , but different time.

At the same time, contrast to the diffraction peak intensity in the graph, it can be observed clearly, with the calcine time increasing, the intensity of the diffraction peaks of samples first increases and then decreases. When calcine time for 8h, the diffraction peak of sample is the sharpest and has the highest intensity, which suggests that its crystallinity of the calcine time at the condition of 8h is the best, while the remaining sample intensity at three different calcine time is weaker than the calcine time of the 8h, and samples of calcine time for 7h, 9h and 10h at 35~40 degrees all have a small diffraction peaks, it is likely that layered structure materials be changed with the calcine time increasing. Therefore, the optimal calcine time of cathode materials in acetic acid system is identified as 8h.

3.3 The electrochemical performance test

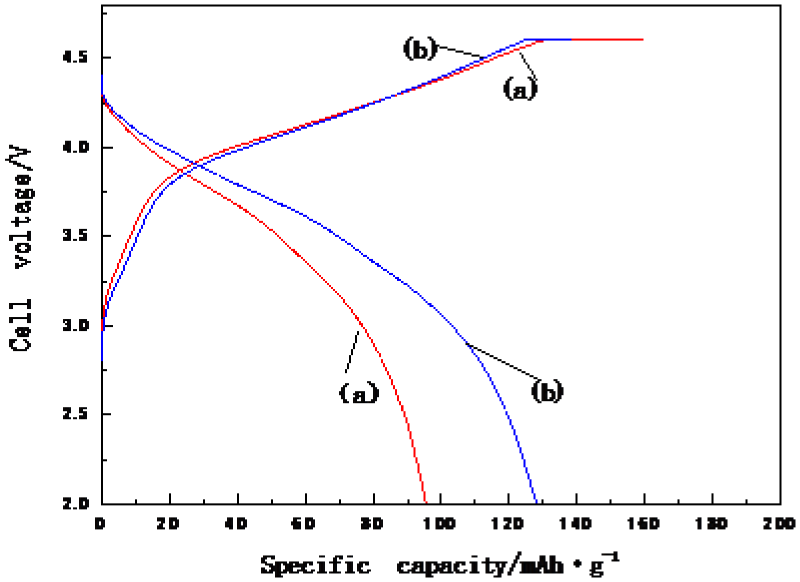

Figure 5. The first(a) and second(b) charge-discharge curves at 0.1C rate

The initial charge and discharge curve in the 0.1 C rate of cathode material Calcined synthesis at 800 ℃ for 8h are shown in Fig. 5. It can be seen from the chart, at the 0.1C current ratio over 4.5 V, an irreversible potential platform of acetic acid cathode material appears in the initial charge process, similarly, the platform is corresponding to a small reversible process off lithium and oxidation (Li_2O). Li_2MnO_3 in the material is activated in the process, making the first discharge process can obtain higher discharge specific capacity.

Meanwhile, we can see from the picture, the first charge and discharge specific capacity of this material is high, and the discharge specific capacity is much lower than its second times, then charge and discharge capacity gap is about 40mAh/g. Thus, the irreversible capacity of the layered rich lithium materials in acetic acid system is large. Therefore , the performance of this system of material in the first charge and discharge is not ideal. Pressed button batteries, test data shows that, although the first charge and discharge are not so ideal, but from the second charge and discharge cycle to the end of it, the effect of charge and discharge become very ideal.

Fig. 6 shows cycle performance and efficiency curve of the cathode materials in acetic acid system. As can be seen from the graph, after charge and discharge cycle test for 20 times the regular capacity retention rate fluctuates obviously. But with the increasing of the times of cycles, the capacity retention rate comes to be smooth, and the capacity retention rate is over 98%. Except the first charge and discharge cycle, the rest 20 times are over significantly 80%. It can be seen from the figure that the first cycle performance is low efficiency, which is only 79.92%, from the following, the capacity retention rates have an increasing trend and are almost up to 90%, which indicates that charge and discharge tests performed at 0.1C rate, the charge and discharge capacity of cathode materials rarely decay. It further proves that this material has excellent charge and discharge cycle performance.

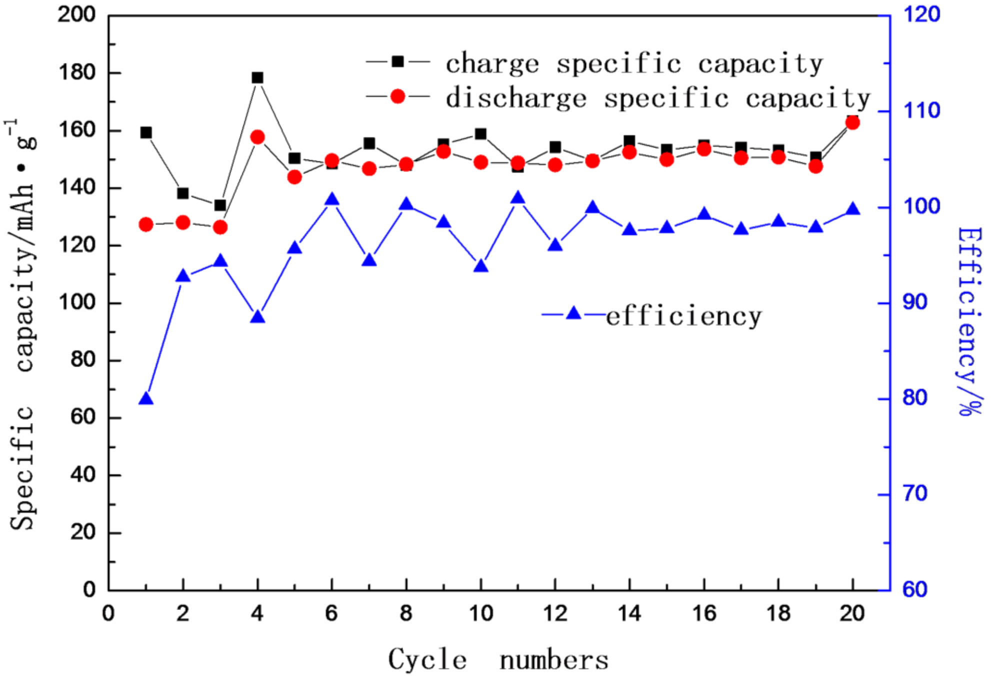

Figure 6. Cycle performance of charge-discharge curves at 0.1C rate

Huang [14] via the coprecipitation method prepared $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ materials, after the testing we can found the first discharge capacity reached 250.7 mAh/g at 0.1C, after 20 cycles the capacity retention rate was 83%,

Tang[15] used sol-gel method synthesized Lithium-rich layered $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ cathode materials, the experimental results show that at 0.1C the first discharge capacity of cathode material is 236.1 mAh/g, after 20 cycles, the capacity retention rate was 91%.

The coprecipitation-calcination method was used by Yu [16] to synthesized $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ cathode materials. The results show that the first discharge capacity of sample was 224.3 mAh/g at 0.1C, the capacity retention rate was 91.8% after 20 cycles.

Table 1. Comparison of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders on their electrochemical properties.

component	Synthesizing method	discharge capacity(mAh/g)	Capacity retention	References
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	coprecipitation method	250.7;0.1C	83%	[14]
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	sol-gel method	236.1; 0.1C	91%	[15]
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	coprecipitation-calcination method	224.3;0.1C	91.8%	[16]
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	Acetate Coprecipitation method	69.54;0.1C	95%	As prepared

4. CONCLUSION

(1)Of different calcine temperature, the diffraction peaks of the sample for 800 ℃ was of the highest intensity and the sharp peak, therefore ,the calcine temperature was identified as 800 ℃.

(2) In the condition of 800 ℃, when the calcine time was for 8h,$Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ had a good crystalline structure, and the material particle was of uniform size, with good layered structure, and no agglomeration,so the calcine time was 8h.

(3)The first charge and discharge capacity of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ at 0.1C rate was161.788mAh/g, the discharge specific capacity was 92.242mAh/g. The gap between the charge and discharge specific capacity was for 69.546mAh/g. Through the 20 cycle tests, the charge and discharge efficiency of materials could be up to 95%.

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