Structural, electrochemical and cycling properties of Nb⁵⁺ doped LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode materials at different calcination temperatures for lithium-ion batteries^{*}

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 $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode material is prepared by sol-gel method and the effects of Nb⁵⁺ doping and different calcination temperatures on cathode materials were deeply investigated. Structural and morphological characterizations revealed that the optimal content of 1 mol% Nb⁵⁺ can stabilize layered structures, mitigate Ni²⁺ migration to Li layers, improve lithium diffusion capacity, and reduce lattice expansion/shrinkage while cycling. And calcination temperature at 800 °C can not only ensure good morphology, but also suppress the mixed discharge of lithium and nickel in the internal structure. Electrochemical performance evaluation revealed that Nb⁵⁺ doping improves the discharge-specific capacity of the material, which is conducive to ameliorating its rate capability and cycle performance. And the material at 800 °C exhibits the highest discharge specific capacity, the best magnification performance, low polarizability, and the best cycle reversibility.

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Because of the high volume, no memory effect, high voltage power density, good cycle performance and excellent safety performance, lithium ion batteries had received wide attention^[1-3]. Notably, the capacity and voltage of lithium batteries are determined by the cathode material. Ternary material $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ (NCM) has the advantages of high specific capacity of LiNiO_2 , good circulation and conductivity of LiCoO_2 , low cost and high safety of LiMnO_2 , which is a promising cathode material^[4,5].

The energy density of NCM cathode material is proportional to the internal nickel content^[6]. NCM811 has the advantages of high energy density and strong endurance. However, due to the high metal activity of nickel, the layered structure of materials is extremely easy to deteriorate and its cycle stability and safety of use also decline^[7], which affects the service life of the battery. Mainly using ion doping, surface coating, single crystallization, pre-oxidation and other methods to modify the ternary cathode material related research^[8], oping is an important means to improve the performance of electrode materials and is widely used in the study of modification of positive electrode materials. Generally, ions with a radius close to that of the ions in the material are doped to make the doped ions enter the lattice, replace some ions in the raw material, and stabilize the crystal structure of the material^[9]. As a transition metal, the bond energy of Nb is 753 kJ/mol, which is higher than that of Ni-O (391 kJ/mol), Co-O (368 kJ/mol), and Mn-O (402 kJ/mol), so Nb⁵⁺ (0.64 Å) is supposed to the most promising dopant among the commonly used doping elements.

In the process of preparing materials, calcination atmosphere, calcination temperature, excess percentage of Li and different complexing agents can affect the structure and cycling performance^[10]. Among these, calcination temperature is an extremely critical factor in the preparation of materials. Low temperature will cause poor crystallinity of the material, incomplete crystal growth. High temperature will cause agglomeration on the material surface. Lithium deficient compounds are formed due to more volatilization of lithium, which increases the impedance value of the material. Accordingly, Nb doped NCM811 was synthesized by sol-gel method, the optimal Nb5+ content is 1 mol%^[11], annealing at 40 °C gradient in air atmosphere, investigating the effects at different calcination temperatures in the range of 760-840 °C on structure, morphology and electrochemical properties of cathode materials.

 $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ was prepared by a sol-gel method with citric acid ($C_6H_8O_7 \cdot H_2O$) as a complexing agent. $Ni(CH_3COO)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $C_4H_6MnO_4 \cdot 4H_2O$,

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LiOH·H₂O and C₆H₈O₇·H₂O were used as the starting materials. First of all, weigh the molar ratio of Ni: Co: Mn is 8: 1: 1, citric acid: m (total metal ions) is 1: 1 and the excess of lithium salt is 5% (make up for the volatilization of lithium salt in the process of high temperature sintering) and Nb₂O₅ was added by the molar ratio of 0.01 compared with the molar sum of Ni, Co and Mn.

After then, cobalt and manganese in deionized water to prepare solution 1, and dissolve citric acid and LiOH·H₂O into transparent solution 2 which is slowly added to solution 1, add ammonia after magnetic stirring evenly in the water bath pot to regulate the pH of the solution to 7—8. Evaporate the solvent at 80 °C for several hours to form a wet gel state and it is dried at 180 °C for 12 h to form a dry gel. After completing the above operations, grind the sample carefully in an air atmosphere, pretreat it at 480 °C for 6 h, cool it to room temperature and take it out and grind it again.

Finally, NCM811 materials were obtained by sintering at 720 °C, 760 °C, 800 °C and 840 °C for 12 h after slightly grinding, which were named Nb-NCM-720, Nb-NCM-760, Nb-NCM-800 and Nb-NCM-840, respectively. Accordingly, the reference sample was calcined at 800 °C without Nb₂O₅, which was named NCM-800.

The crystal structure of the material was determined by X-ray diffraction (XRD UitimaIV), and then the diffraction intensity data of the measured samples were further analyzed and calculated to quantify the phase composition of the samples. Cu rotating target is used, scanning range 2θ =10°—80°, scanning speed 0.1 s/step, step size 0.02°, voltage 40 kV, current 200 mA, and the obtained data were analyzed by Origin software. The surface morphology of the material was observed using a scanning electron microscope (SEM 460L03040702); the elemental content changes on the surface of the cathode material before and after the modification were analyzed using a field emission gun (Quanta-feg250) on an energy spectrometer (EDS 460L03040702) on an SEM.

CR2016 coin cell was fabricated to measure the electrochemical characterization of the cathode material. The cathode electrode slurry was prepared by thoroughly mixing LiNi_{0.8-r}Co_{0.1}Mn_{0.1}Nb_rO₂ material (x=0.01,80 wt%), acetylene black (10 wt%) and polyvinylidene fluoride (PVDF) binder (10 wt%) in N-methyl pyrrolidone (NMP). After stirring in a stirrer, it is evenly applied to the aluminum foil, put the coated electrode into the oven and dry it at 80 °C for 2 h, then move it to the vacuum drying oven and dry it at 120 °C for 12 h. Lastly, 11 mm diameter disks were punched with cathode electrodes. The positive electrode shell, positive electrode sheet, electrolyte, diaphragm (Celgard 3501), electrolyte (1M LiPF6-EC/DMC/EMC (1: 1: 1, v/v/v)), anode (lithium metal disc), gasket, shrapnel, and negative electrode shell are assembled in the order from bottom to top, and the button cell is put into the sealing machine for sealing.

At room temperature of 25 °C, within the voltage range of 2.75–4.5 V, use the battery tester (LAND

CT2001A) to conduct the initial charge/discharge test on the sample, and observe the initial charge/discharge specific capacity; discharge cycles for each sample at different current densities to test the multiplicative performance; perform 100 charge/discharge cycles on the sample, test the cycling performance and calculate the capacity retention rate of the sample. Cyclic voltammetry (CV) analysis of the material was performed using an electrochemical workstation (CHI660D) at a scanning rate of 0.1 mV/s to analyze the degree of polarization and cyclic reversibility.

As shown in Fig.1, all samples have similar diffraction patterns, which are single-phase materials of a-NaFeO2 layered rock salt structure^[12]. There is no impurity phase, and the peak shape is narrow and sharp, indicating that each sample has a good degree of crystallization. The diffraction peak pairs of I(006)/I(102) and I(108)/I(110)at 38° and 65° are obviously separated, indicating that the sample has formed a highly ordered layered structure. The peaks of I(003) and I(104) move slightly to the lower 2θ angle in Fig.1(a), due to the large influx of Nb⁵⁺ during calcination, implying that Nb⁵⁺ has been successfully mixed into the lamellar structure of the sample. Meanwhile, at the 800 °C, the splitting peaks corresponding to I(006)/I(102) and I(108)/I(110) of the sample is getting narrower and become more obvious, which means dopant material has a better hexagonal layered composition and more saturated crystallinity^[13].

Tab.1 summarizes the unit parameters calculated by Origin software. Generally c/a is used to characterize the layered structure of the material, the larger the ratio, the better the layered structure and the less cation mixing^[14]. Obviously the c/a ratio of the materials is greater than 4.899 0. But the values of c/a of doped samples are slightly higher than those of bare sample, indicating Nb substitution has improved the degree of ordering and crystallinity of the layered structure. Discuss the temperature accordingly, both c and a axes increase with increasing the calcination temperature, and the cell volume also increases monotonously from 101.434 Å³ to 101.868 Å³. Nevertheless, the c/a value, an indicator of the degree of the hexagonal structure order, is almost the same.





Fig.1 (a) XRD patterns of NCM-800 and Nb-NCM-800 samples; (b) XRD patterns of Nb-NCM-720, Nb-NCM-760, Nb-NCM-800 and Nb-NCM-840 samples; (c) Enlarged (003) peaks; (d) Enlarged (104) peaks

Generally, c/a is used to characterize the layered structure of the material^[15]. Tab.1 summarizes the related parameters calculated by Origin software. All materials have a c/a ratio greater than 4.899 0, indicating good crystallinity and layered structure. The values of c/a of Nb-NCM-800 are slightly higher than those of NCM-800. It is possible that the surface of the material is doped with a very small amount of Nb ions, which improved the stability of the internal structure. With the temperature rises, there are some changes of the c axis and a axis correspondingly and the cell volume tends to increase monotonously. However, the c/a values, which are indicators of the orderliness of the hexagonal structure, are basically not different.

Li⁺ and Ni²⁺ in the material have similar ionic radii leading to cation mixing easily. The value of I(003)/I(104) is used to characterize the cation miscibility of the material^[16]. It can be found that the value of I(003)/I(104) of doped samples is significantly higher than that of bare samples in Tab.1, indicating that niobium doping does inhibit cation disorder, which effectively enhances the transfer ability of lithium ions. With the temperature increasing to 840 °C, I(003)/I(104)strength ratio increases first and then decreases. With low calcination temperatures, the energy provided to low-priced elements to break through the energy barrier and oxidize to high prices is not enough, resulting in incomplete crystallization of the material. And calcined at 800 °C, Nb-NCM-800 has the highest ratio of 1.45, the mixing degree of anions is the lowest, and the transportation of lithium ions is the most efficient, because Ni²⁺ turns into Ni³⁺ by oxidation reaction, which reduces the disorder of cations. At 840 °C, the ratio drops significantly, and high temperature causes secondary crystallization of the crystal and intensifies the mixed discharge of cations^[17].

Tab.1CrystallographicparametersofNCM-800,Nb-NCM-720,Nb-NCM-760,Nb-NCM-800andNb-NCM-840 samples

Samples	a (Å)	c (Å)	c/a	$V(Å^3)$	<i>I</i> (003)/ <i>I</i> (104)
NCM-800	2.873 1	14.202 6	4.943 3	101.541	1.36
Nb-NCM-720	2.872 5	14.196 2	4.942 1	101.434	1.31
Nb-NCM-760	2.873 7	14.213 9	4.946 2	101.652	1.38
Nb-NCM-800	2.875 4	14.226 6	4.947 5	101.713	1.45
Nb-NCM-840	2.874 8	14.211 3	4.943 4	101.868	1.40

As shown in Fig.2(c) and (d), the materials have homologous morphology and good crystalline particles similar to spheres, which shows the incorporation of Nb⁵⁺ didn't alter the original morphological structure of NCM811. Compared with the doped material, the original material contains some sub-micron particles, which shows a slightly larger agglomeration. The dimensions of both are similar to the raw material, but the doped material has a more uniform and smooth morphology.

As shown in Fig.2(a), (b), (c) and (e), the size of the particle gradually grows with the increase of sintering temperature. Particles calcined at 720 °C possess uneven size and irregular shape with inconspicuous reunion and there is a tendency for primary particles to grow. With the temperature increase to 800 °C, there are significant changes in the morphology of the primordial particles. Additionally, the secondary particles have a uniform shape similar to a sphere, and each of them is composed of numerous primary grains with excellent dispersibility and crystallinity, and electrode performance is considered to be the best with this particular morphology. After further calcined at 840 °C, the crystal grows evidently, the size further increases and the surface becomes relatively rough.

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Lithium element volatilizes seriously at high temperature, forming lithium deficient compounds on the material surface, which aggravates the agglomeration of the material. The larger secondary particles hinder the diffusion of Li^+ . Therefore, the cathode material has the best morphological characterization at the calcination temperature of 800 °C.

The EDS image of doped material is shown in Fig.3. It is clear that the Ni, Co, Mn and Nb are distributed homogeneously in the doped sample.



Fig.2 SEM images of (a) Nb-NCM-720, (b) Nb-NCM-760, (c) Nb-NCM-800, (d) NCM-800, and (e) Nb-NCM-840 samples at different magnifications

Fig.4(a) shows the initial charge-discharge curves of during cycling at a 0.1C rate with the voltage range of 2.75—4.5 V. All the curves show a typical smooth shape, which confirms that the layered structure of the material has not changed and there is hardly any obvious polarization. That illustrates when 1 mol% Nb⁵⁺ is doped, the charge specific capacity of the sample is almost unchanged, but the discharge specific capacity is significantly improved. That shows that niobium doping replaces Mn ions, reduces the mixed discharge of Li⁺ / Ni²⁺, inhibits the disorder of cations, and enhances the specific charge-discharge capacity of cathode materials.

Refer to Tab.2 and Fig.4(b) for analysis, the material shows poor electrochemical performance at 720 $^{\circ}$ C, which is attributed to the incomplete growth of the material, it agglomerates on the surface of the material and the mixed discharge of cations is relatively high. With the temperature increasing to 760 $^{\circ}$ C, the initial discharge specific capacity of cathode material increases obviously. The cathode material has the best perform-



Fig.3 EDS elemental mapping for (a) Ni, (b) Co, (c) Mn, (d) O, and (e) Nb of Nb-NCM-800 sample

ance of the first charge-discharge curve at 800 °C, initial discharge specific capacity is the highest among all the samples, and the coulomb efficiency of the sample is greater than 93%. In this state, the mixing degree of cations in the material is the minimum, which is conducive to the transportation of lithium ions. Further rising the annealing temperature to 840 °C, the initial discharge specific capacity showed a downward trend, and the initial coulomb efficiency decreased to 82.4%. It shows that the material has a certain cation mixed discharge at 840 °C. High temperature will cause the lithium salt to volatilize more and form lithium-deficient compounds, the increase in charge transfer impedance, resulting in low discharge performance of the material^[18].

Rate performance is an important index of the energy storage capacity of lithium batteries. The specific discharge capacity was tested at 2.75-4.5 V under different present densities (0.2C, 0.5C, 1C, 2C and 0.2C) and five tests were performed at each rate. Observing the trend of Fig.5, the capacitance loss of the material gradually increases and the difference in capacitance loss is more obvious as current density continues to increase. The discharge capacity of Nb-NCM-800 at 2C (cycle 5) is 78.4% of that at 0.2C (cycle 5) and the discharge capacity of NCM-800 at 2C (cycle 5) is 64.2%. The performance of the former is obviously better than that of the latter. When the current density recovers to 0.2C again, the discharge capacity of Nb-NCM-800 recovers to 158.1 mAh/g, which is close to the initial discharge capacity. In contrast, the discharge capacity of NCM-800 at 0.2C for the second time is significantly lower than that for the first time. It shows that Nb doped cathode materials have more superiority rate performance.

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Fig.4 (a) Charge-discharge curves of NCM-800 and Nb-NCM-800 samples; (b) Charge-discharge curves of Nb-NCM-720, Nb-NCM-760, Nb-NCM-800 and Nb-NCM-840 samples

Tab.2 Charge/discharge capacities of the samples obtained from initial charge-discharge curve

Samples	Initial charge capacity (mAh/g)	Initial-discharge capacity (mAh/g)	Coulombic efficiency (%)
NCM-800	208.3	186.4	89.5
Nb-NCM-720	183.8	158.5	86.2
Nb-NCM-760	213.2	192.6	90.1
Nb-NCM-800	211.5	201.8	93.3
Nb-NCM-840	218.1	179.7	82.4

Compared with other samples in Fig.5(b), Nb-NCM-720 and Nb-NCM-760 show the lowest specific discharge capacity, which is attributed to the incomplete growth of the material and the maturity of primary particles is not enough, which hinders the diffusion of Li⁺. The material at 800 °C has the best rate capability, indicating that Nb-NCM-800 has low polarizability and good cycle reversibility. This attributes to the lower cationic discharge of layered materials at 800 °C. As a result, Li⁺ diffuses between active particles and electrolytes more rapidly^[19], increasing the conductivity of ionic and electronic. The rate performance of Nb-NCM-840 decreases, whose reason may be the formation of large particles at higher temperatures leads to the extension of the lithium diffusion path and the deterioration of the

electrical properties of the material.



Fig.5 (a) Discharge capacities at various C-rates of NCM-800 and Nb-NCM-800 samples; (b) Discharge capacities at various C-rates of Nb-NCM-720, Nb-NCM-760, Nb-NCM-800, and Nb-NCM-840 samples

At 2.8—4.5 V, test the cycling performance of the sample in Fig.6. All materials are cycled 100 times at a current rate of 0.5C. With cycle-index increases, the volume retention rate of all samples decreases in varying, because repeated charging and discharging reduce the active surface area of the electrode, increase the current density and polarity, and the lattice in the cathode material collapses or is blocked, reducing the storage bits that can store Li^+ back and forth. Moreover, the inert substances in the electrochemical reaction inside the lithium battery destroy the capacity balance between electrodes, resulting in irreversible capacity loss of the battery capacity.

As shown in Tab.3, after 100 cycles, the capacity retention rate of Nb-NCM-800 is 78.8%, which is 10.4% higher than that of NCM-800. The increase in capacity retention rate is attributed to Nb⁵⁺ stabilizing the internal structure and alleviating the phase transition process from layered structure to rock salt structure, indicating that appropriate niobium substitution is conducive to improving the cycling performance of NCM811^[20].

Due to the low calcination temperature and incomplete material reaction, Nb-NCM-720 has the lowest specific discharge capacity all along. Significantly, Nb-NCM-760 has optimal discharge specific capacity initially. The reason is that the particle radius is small at 760 °C and the overall contact surface area is relatively large, which increases the interface contact area of the electrochemical reaction inside the material, therefore the material has better cycle stability. But after more than 50 cycles, its specific capacity drops sharply because of its unstable layered structure. Nb-NCM-840 has the worst capacity retention and capacity loss of 32.32%, which is due to the abnormal growth of primary particles and serious agglomeration at high temperatures, which increases the diffusion path and charges transfer impedance of Li⁺. Compared with other samples, the electrode is relatively stable at 800 °C, and the oxidation decomposition of the positive active material to the electrolyte is relatively small under the charging state, which has the smallest specific discharge capacity attenuation.



Fig.6 (a) Cycling performance curves of NCM-800 and Nb-NCM-800 samples; (b) Cycling performance curves of Nb-NCM-720, Nb-NCM-760, Nb-NCM-800, and Nb-NCM-840 samples

Due to the low calcination temperature and incomplete material reaction, Nb-NCM-720 has the lowest specific discharge capacity all along. Significantly, Nb-NCM-760 has optimal discharge specific capacity initially. The reason is that the particle radius is small at 760 °C and the overall contact surface area is relatively large, which increases the interface contact area of the electrochemical reaction inside the material, therefore the material has better cycle stability. But after more than 50 cycles, its specific capacity drops sharply because of its unstable layered structure. Nb-NCM-840 has the worst capacity retention and capacity loss of 32.32%, which is due to the abnormal growth of primary particles and serious agglomeration at high temperatures, which increases the diffusion path and charges transfer impedance of Li⁺. Compared with other samples, the electrode is relatively stable at 800 °C, and the oxidation decomposition of the positive active material to the electrolyte is relatively small under the charging state, which has the smallest specific discharge capacity attenuation.

Tab.3 Discharge capacity retention of the samples after 100 cycles

Samples	Dischar	ge specific capacity (mAh/g)	Capacity reten-
	First	Last	tion (%)
NCM-800	175.5	120.1	68.43
Nb-NCM-720	150.3	115.5	76.85
Nb-NCM-760	180.7	125.2	69.28
Nb-NCM-800	176.7	139.2	78.78
Nb-NCM-840	161.8	109.5	67.68

CV is a commonly used electrochemical research method. Fig.7 displays the curves of the first three cycles of different materials at the scanning speed of 0.1 mV/s. All samples have three pairs of redox peaks with complete peak types, corresponding to H1 \rightarrow M, M \rightarrow H2 and H2 \rightarrow H3 phase transitions, respectively. There is no oxidation/reduction peak near 3 V, explaining the valence of manganese remains unchanged in the material, and the effect of Mn⁴⁺ is only to stabilize the structure.

The deviation from the first redox peak to the high voltage is due to the formation of SEI film in the material and some phase transitions during charging and discharging. There is no significant change in the position of the reduction peak in the last two cycles, the first pair of reduction peaks is at the position of 3.6-3.8 V, corresponding to the transformation of Ni²⁺/Ni⁴⁺; the second pair of reduction peaks is at the position of 3.9-4.0 V, corresponding to the transformation of Ni³⁺/Ni⁴⁺; the third pair of reduction peaks is about 4.2 V, corresponding to Co³⁺/Co⁴⁺ conversion. In addition, the images of all samples after two cycles can roughly coincide, indicating that the material has excellent cycle reversibility. In contrast between bare and Nb⁵⁺ doped materials, the similar oxidation/reduction peaks indicate that doping Nb⁵⁺ didn't affect the electrochemical reaction significantly during charge and discharge.

The corresponding peak potential difference DE ($E_{oxi-dation}-E_{reduction}$) is usually used to explain the cyclic reversibility and the degree of polarization of the material^[21]. A large *DE* between the peak oxidation/reduction voltage means a more severe polarization of the electrode^[22]. The potential difference of NB-NCM-800 is less than that of NCM-800, indicating that doping Nb⁵⁺ can inhibit the electrochemical polarization and improve

the cycle reversibility of materials. Compared with other samples, the last two cycles of Nb-NCM-800 have the best overlap and the smallest potential difference, which explains that the material has the smallest electrode polarization and the highest reversible electrochemical activity at the calcination temperature of 800 °C.





Fig.7 Cycling performance curves of (a) NCM-800, (b) Nb-NCM-800, (c) Nb-NCM-720, (d) Nb-NCM-760, and (e) Nb-NCM-840 samples

In this paper, LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode materials were synthesized by the sol-gel method. The effects of niobium doping at different calcination temperatures of 720 °C, 760 °C, 800 °C and 840 °C on the structure, morphology and electrochemical properties were investigated in detail. The results show that Nb⁵⁺ substitution presents better morphology characterization, inhibits cation disorder, and improves the stability of the layered structure at the calcination temperature of 800 °C. Within the voltage range of 2.75-4.5 V, during the initial charge/discharge test at a rate of 0.1C, Nb-NCM-800 shows the optimal discharge specific capacity is 201.8 mAh/g. When the discharge specific capacity is tested at different current densities (0.2C, 0.5C, 1C, 2C and 0.2C), Nb-NCM-800 shows the best rate performance. After 100 cycles, the capacity retention rate of Nb-NCM-800 is 78.8%, showing the best cycle reversibility. When analyzing the first three cycles of CV curves of the material at the scanning speed of 0.1 mV/s, Nb-NCM-800 also has the best overlap and the smallest potential difference, indicating that it has the smallest electrode polarization and the highest reversible electrochemical activity.

Ethics declarations

Conflicts of interest

The authors declare no conflict of interest.

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