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Effect of calcination temperature on characteristics of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode for lithium ion batteries

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Abstract: $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was synthesized by sol-gel method and effect of calcination temperature on characteristics of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode was investigated. The structure and characteristics of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ were determined by XRD, SEM and electrochemical measurements. The results show that the compound $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ has layered structure with hexagonal lattice. With the increase of calcination temperature, the basicity of the material decreases, and the size of primary particle rises. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ calcined at 900 ℃ for 12 h shows excellent electrochemical performances with large reversible specific capacity of 157.5 mA·h/g in the voltage range of 2.75−4.30 V and good capacity retention of 94.03% after 20 charge/discharge cycles. Capacity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ increases with enhancement of charge voltage limit, and specific discharge capacities of 179.4 mA·h/g, 203.1 mA·h/g are observed when the charge voltages limit are fixed at 4.50 V and 4.70 V, respectively.

Key words: lithium ion battery; $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$; sol-gel; cathode

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1 Introduction

Lithium ion batteries (LIB) have been widely used in portable appliances because of a favorable combination of voltage, energy density, cycling performance, and have developed rapidly during the past decade[1−3]. $LiCoO_2$ is the primary cathode material in commercial lithium ion battery because it is reasonably easy to synthesize and has excellent electrochemical properties[4]. But due to its high cost and toxicity, an intensive research for new cathode materials have been underway in recent years[5−7].

Among these new cathode materials for replacing $LiCoO_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is a prospective cathode material for its low cost, large capacity, good thermal stability and excellent cycling performance[8−9]. Intensive research is conducted on the compounds and many developments have been achieved[10−12]. It has been found that $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ has a hexagonal α-$NaFeO_2$ crystal structure with a space group of R3m, and it is a promising candidate electrode material for use in hybrid-electric vehicles[13−15]. However, there are some problems in this compound such as low packing density and unsatisfactory safety. They are related with the structure and surface properties, which is much dependent on the preparation method and calcination temperature.

The aim of this work is to synthesize $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode by sol-gel method, clarify the effects of calcination temperature on the structure and electrochemical properties of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode, and optimize the calcination temperature.

2 Experimental

All the samples of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ were synthesized by the citric acid sol-gel method. Stoichiomeric amounts of $LiNO_3$, $Mn(CH_3COO)_2.4H_2O$, $Ni(CH_3COO)_2.4H_2O$, and $Co(CH_3COO)_2.4H_2O$ were dissolved in distilled water. Citric acid was used as a chelating agent. The solution pH was adjusted to 6−7

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with ammonium hydroxide. The solution was heated at 60−80 ℃ until a transparent sol was obtained. The resulting gel precursor was heated at 250 ℃ for 2 h in air and followed with decomposition at 450 ℃ for 5 h to remove the organic contents. The decomposed powders were ground, pressed into pellets and calcined at different temperatures in air for 12 h. The heating rate of the powder was 2 ℃/min.

X-ray powder diffraction (XRD) measurements were made with a Rigaku diffractometer. Scanning electron micrographs (SEM) were obtained with a JEOL JSM-5600LVspectrometer. Brunauer-Emmer-Teller(BET) surface area measurements were made using a Quantac-grome monosorb surface area analyzer.

The pH of the products was characterized as follows. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powder was added into distilled water with mass ratio of 1:50, and the mixture was stirred for 10 min. Then the solid was removed by filtration, and pH of the solution was examined with a Mettler Toledo Lp115 pH meter.

The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ compound was mixed with acetylene black as electric conductor and poly(vinylidene difluoride) (PVDF) as binder. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode was prepared by spreading the above mixture on aluminum foil. Charge-discharge tests of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrodes were performed in coin cells with $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathodes and lithium anodes. A UP 3025 porous membrane of 25 μm in thickness was used as a separator, and the electrolyte was 1 mol/L $LiPF_6$ dissolved in a mixture of ethylene carbonate(EC), dimethyl carbonate(DMC) and methyl-ethyl carbonate(EMC) with a volume ratio of 1:1:1. The charge/discharge characteristics and cycling performance of coin cells were investigated.

3 Results and discussion

Fig.1 shows the SEM images of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples. The sample calcined at 750 ℃ reveal the loose, disordered primary particles. With the increase of calcination temperature, the primary particles tend to sinter into tight, smooth particles, and the particle size

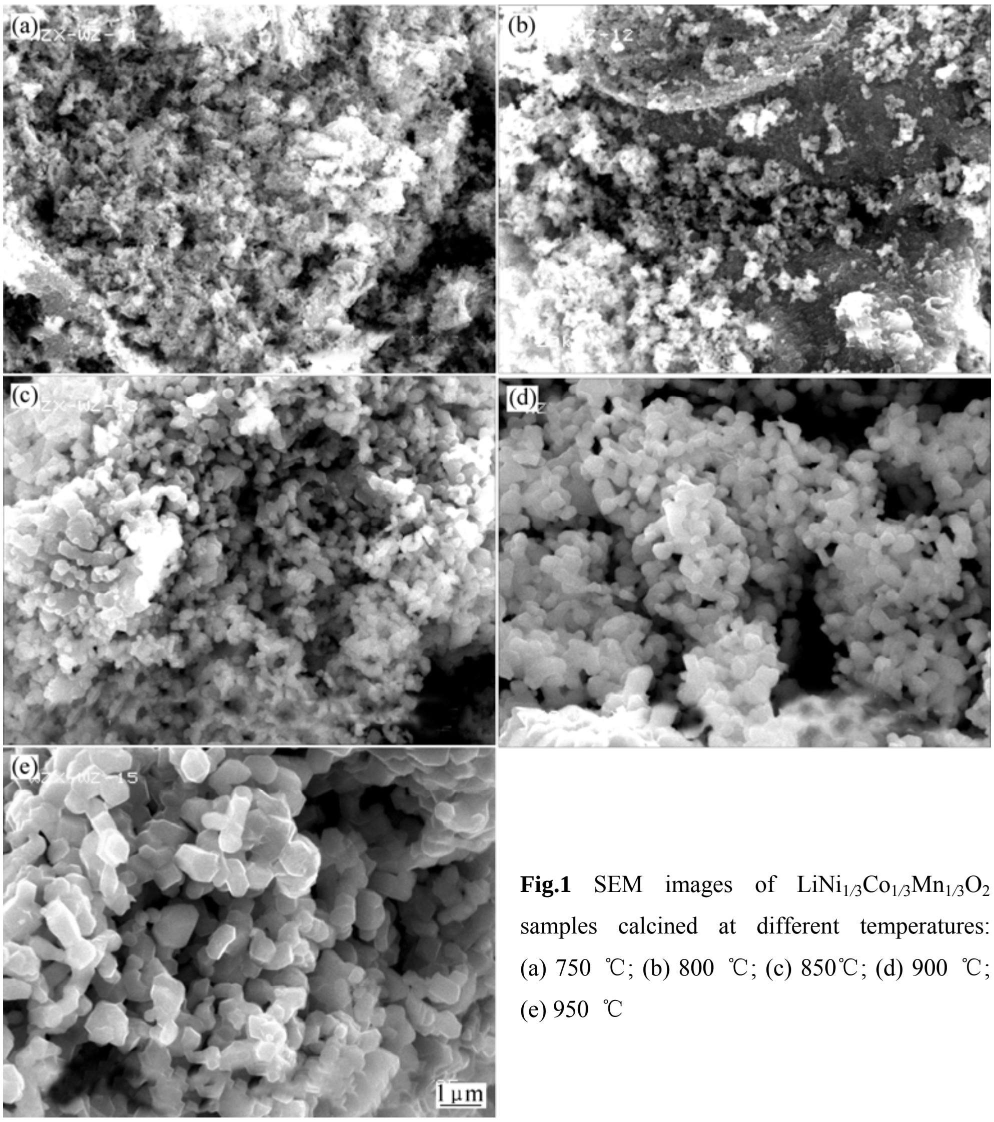

Fig.1 SEM images of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples calcined at different temperatures: (a) 750 ℃; (b) 800 ℃; (c) 850℃; (d) 900 ℃; (e) 950 ℃

rises. The sample calcined at 950 ℃ reveals well developed primary particles with quite smooth surface and particle size of 0.5−1 μ m.

The X-ray diffraction patterns of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples are shown in Fig.2. The XRD patterns of the samples are similar to that of $LiCoO_2$ (α-$NaFeO_2$ type, space group R3m) and can be indexed as hexagonal lattice. The transition metal atoms (M=Ni, Co, Mn) are supposed to be randomly distributed on the 3b sites, whereas the lithium atoms occupy the 3a sites and O atoms occupy the 6c sites. No obvious impurity phase peaks can be observed, indicating that the synthesized samples are single phase. In XRD patterns, the splitting of (006)/(102) peak and (018)/(110) peak are regarded as the indications of characteristic of layered structure materials[15]. From the observation of peak splitting of (006)/(012) and (018)/(110) near 38° and 65°, respectively, it can be seen that the layered structure is well developed[5]. The peak splitting in the XRD pattern of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ synthesized at 900 ℃ is more obvious than that of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ synthesized at 800 ℃, indicating that layered structure is better when the calcination temperature is higher.

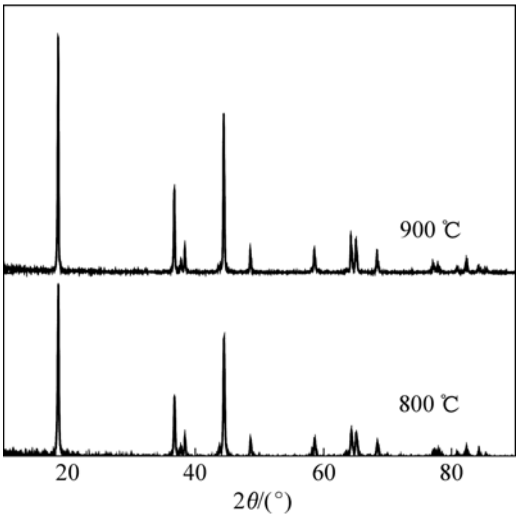

Fig.2 X-ray diffraction patterns of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples synthesized at different temperatures

Fig.3(a) shows the pH of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ versus calcination temperature. As the calcination temperature increases, the pH of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ decreases. It can be observed that the pH falls quickly in the range of 750−850 ℃ and declines slightly in the range of 850−950 ℃. The basicity of the sample is mainly related to the lithium that does not enter into the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ crystal, so it can be concluded that the lithium compound reacts more completely with the transitional metal compounds at high temperature. As shown in Fig.3(b), the dependence of BET surface area on the calcination temperature is similar to that of pH. For the sample synthesized at 750 ℃, BET specific surface area is 10.64 m^2/g. With increasing the calcination temperature from 850 to 950 ℃, BET specific surface areas are quite low in the range of 1.22–3.58 m^2/g and tend to decrease. It can be attributed to the better development of the primary particles at higher temperature, which is shown in Fig.1.

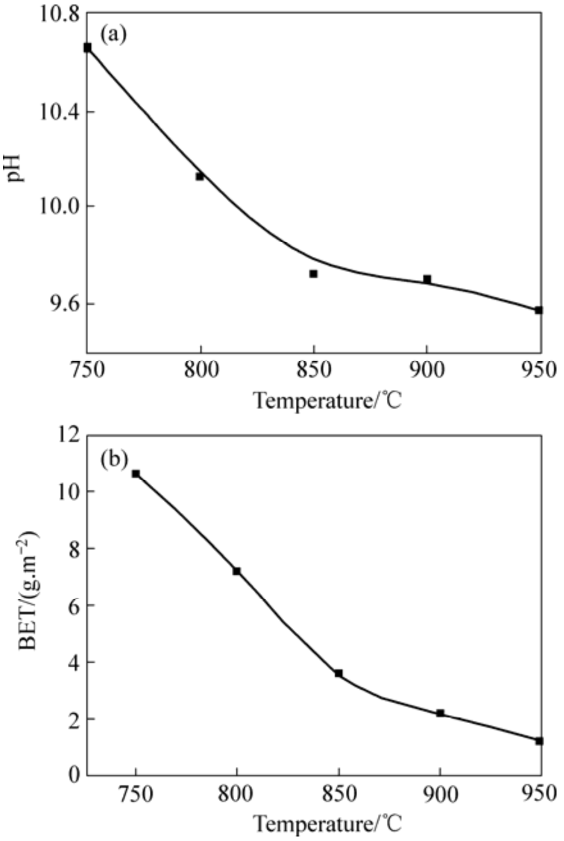

Fig.3 Effect of calcination temperature on pH(a) and BET specific surface(b) of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

Fig.4 shows the initial discharge curves for $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples calcined at different temperatures. They were measured at a current of 30 mA per gram of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ between 2.75 and 4.3 V. All the profiles show the single plateaus with an average voltage near 3.8 V. The discharge capacity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ rises with increase of calcination temperature in the range of 750−900℃. However, a significant discharge capacity fading was observed for the sample calcined at 950 ℃. The sample calcined at 900 ℃ gives the largest discharge capacity of 157.5 mAh/g. To illustrate the process more clearly, the relationships between differential capacity (d*C*/d*V*) and voltage are given in Fig.4(b). There is an appearance of only one reduction peak centered at 3.75 V. As the calcination temperature increases from 750 ℃ to 900 ℃, the redox peak becomes narrow and the height gradually rises, which suggests that the discharge voltage becomes stable and flat, and it is consistent with the discharge curves shown in Fig.4(a).

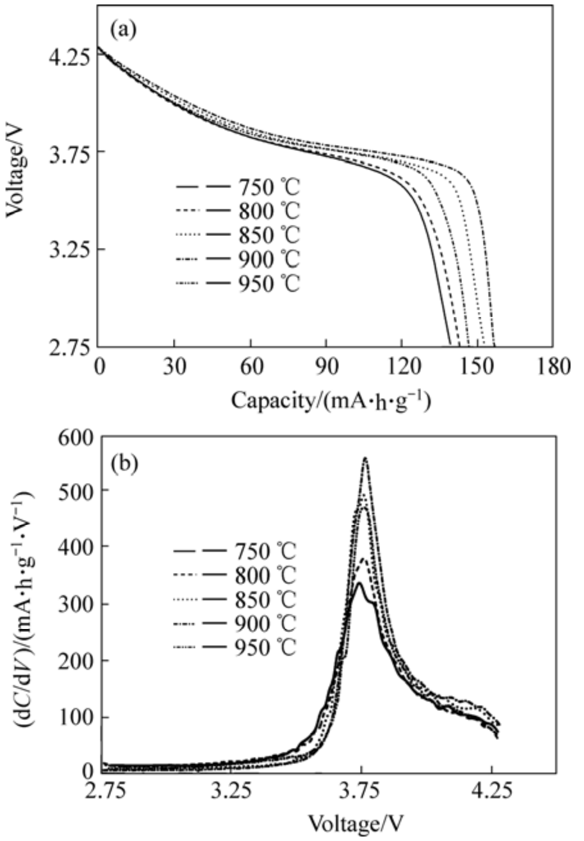

Fig.4 Initial discharge characteristics of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples calcined at different temperatures: (a) Voltage vs capacity profiles; (b) Differential capacity vs voltage profiles

The cycling performance of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathodes was measured at a current of 30 mA per gram of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ between 2.75 and 4.3 V. Fig.5 indicates that the cycling performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples is improved with increasing the calcination temperature. After 20 charge-discharge cycles, the samples synthesized at 900 ℃ and 950 ℃ exhibit good cycling performance with capacity retention ratio of 94.03% and 94.36%, respectively. The improvement of the cycling performance at higher temperatures correlates with the change in the structure and surface properties.

In order to observe electrochemical performances at higher voltage, the upper cut-off voltage was changed to 4.5 and 4.7 V. The discharge capacities increase obviously by raising the upper cut-off voltage limit, which is listed in Table 1. As to the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ synthesized at 900 ℃, in the voltage ranges of 2.75−4.30, 2.75−4.50 and 2.75−4.70 V, the discharge capacities of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode are 157.5, 179.4 and 203.1 mA·h/g, respectively.

Fig.6 shows the discharge voltage curves and the differential capacity vs voltage curves for the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/Li cell at different upper cut-off

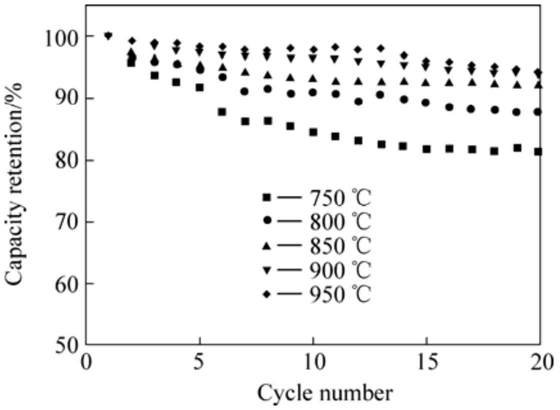

Fig.5 Cycling performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples

Table 1 Discharge capacity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ at different upper cut-off voltage limits

Temperature/℃	Discharge capacity/(mA·h·g⁻¹)		
	4.30 V	4.50 V	4.70 V
750	139.8	152.2	170.9
800	143.5	155.3	176.1
850	153.5	174.1	198.7
900	157.5	179.4	203.1
950	147.2	166	190.3

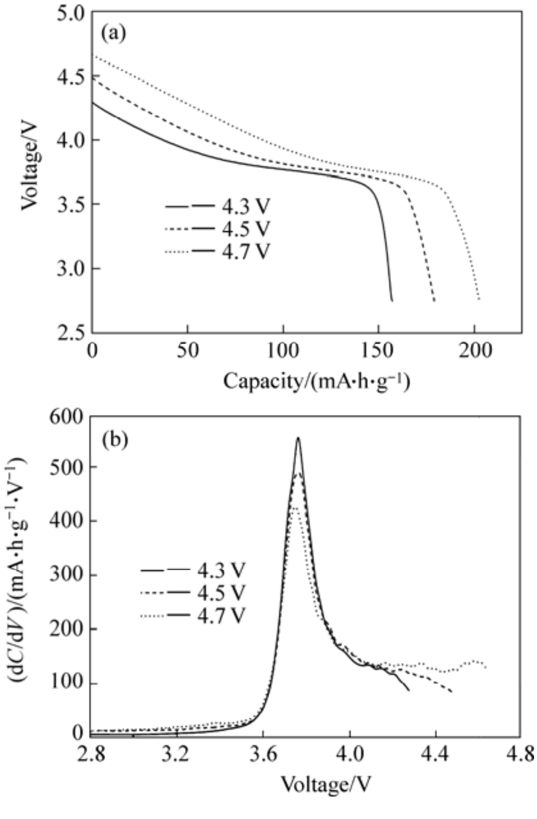

Fig.6 Voltage curves(a) and differential capacity vs voltage curves(b) for $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/Li cell changing upper cut-off voltage limit

voltage limits, the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode was calcined at 900 ℃ for 12 h in air. When the upper cut-off voltage limit increases from 4.30 V to 4.70 V, the discharge capacity is improved by 29.0%, the differential capacity peak around 3.80 V shifts a little to higher voltage, however, the height of the peak declines. This suggests that the increase of discharge capacity is mainly due to the redox reaction occurring at higher voltage.

4 Conclusions

1) Layered structure $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was synthesized by the citric acid sol-gel method. With the increase of calcination temperature, the primary particles of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ exhibit tight, smooth surface and large primary particle size, and the BET specific surface area and pH of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ decrease.

2) The discharge capacity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ rises with increase of calcination temperature in the range of 750−900 ℃. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ calcined at 900 ℃ for 12 h shows excellent electrochemical performances with large reversible specific capacity of 157.5 mA·h/g in the voltage range of 2.75−4.30 V and good capacity retention ratio of 94.03% after 20 charge/discharge cycles.

3) The discharge capacities increase obviously by raising the upper cut-off voltage limit. Specific discharge capacities of 179.4 mA·h/g and 203.1 mA·h/g are observed for $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathodes synthesized at 900 ℃ when the charge voltage limits are fixed at 4.50 V and 4.70 V, respectively.

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