

Synthesis and characterization of layered $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ cathode materials by spray-drying method

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Received 14 April 2006; accepted 21 December 2006

Abstract: Spherical $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ was prepared via the homogenous precursors produced by solution spray-drying method. The precursors were sintered at different temperatures between 600 and 1 000 °C for 10 h. The impacts of different sintering temperatures on the structure and electrochemical performances of $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ were compared by means of X-ray diffractometry(XRD), scanning electron microscopy(SEM), and charge/discharge test as cathode materials for lithium ion batteries. The experimental results show that the spherical morphology of the spray-dried powers maintains during the subsequent heat treatment and the specific capacity increases with rising sintering temperature. When the sintering temperature rises up to 900 °C, $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ attains a reversible capacity of 153 mA·h/g between 3.00 and 4.35 V at 0.2C rate with excellent cyclability.

Key words: spherical $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ powder; synthesis; characterization; spray-drying method; lithium ion battery

1 Introduction

LiCoO_2 is widely used in commercial lithium-ion batteries. During the past decade, lithium-ion batteries with LiCoO_2 and graphite have been developed to a quite high level. However, the toxicity and high cost of LiCoO_2 basically restrict its application in future. Several cathode materials, such as LiMn_2O_4 , LiNiO_2 , LiMnO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ and $\text{Li}(\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x)\text{O}_2$ have been intensively proposed as possible alternatives to LiCoO_2 [1–8]. $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ can be regarded as a special case in which x is 1/3 in $\text{Li}(\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x)\text{O}_2$ system[9]. It was reported that $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ showed a specific capacity of 160 mA·h/g over 2.5–4.4 V[10]. Due to the stable cycling performances, safety and good rate capability of $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$, this material is considered to be one of the best candidates of positive electrode material to replace LiCoO_2 .

Selecting synthetic method plays a very important role in preparing phase-pure, spherical and homogeneous $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$. Solid-state reaction at high temperature is the traditional method for synthesizing cathode materials. However, homogenous composition oxide particles with good morphology are difficult to obtain. $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ is usually synthesized by

the mixed hydroxide method[11–12], in which a $\text{M}(\text{OH})_2$ ($\text{M}=\text{Ni}, \text{Co}, \text{Mn}$) precursor is precipitated from a metal nitrate/vitriol solution and is then reacted with a lithium salt at elevated temperature. This is not difficult in practice, but pH value, temperature, flow conditions, concentrations, and other factors that influence the crystal structure, purity, and physical properties of the products, must be carefully controlled for optimum electrochemical performance[12].

Recent studies and development have shown that spray drying can produce fine spherical particles with high homogeneity and good morphology[13–17]. In this study, spray-drying method was used to produce the precursor, followed by the calcination at different temperatures to prepare $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ powder. The effects of different sintering temperatures on the structure and electrochemical performances of samples were also studied.

2 Experimental

The samples of target compositions $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ with excess amounts of lithium between 0 and 5% were synthesized by the following method. The stoichiometric amounts of LiNO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were used as the

starting materials and dissolved in distilled water. Polyvinyl alcohol(PVA) was dissolved in a separate container and used as a polymeric carrier in a mixed cation nitrate solution, which involved the formation of complexes between the cations and the hydroxyl side groups of PVA, thereby limiting the fractional precipitation of metal nitrate salts. Two kinds of aqueous solutions were mixed into a brown transparent solution, which was fed into a spray drying instrument to produce homogenous precursors. Then it was atomized via a nozzle with two flows at an air pressure of 0.4 MPa, and was dried by hot air. The overall flow rate of solution must be controlled at 10 L/h. The inlet hot air temperature reached 350 °C, and the exit hot air temperature was 150 °C. The as-prepared precursor powders were finally sintered in air at temperatures between 600 and 1 000 °C for 10 h.

The thermal evolution of the mixed precursor was studied by Mettler Toledo TGA/SDTA851e analysis. The samples were characterized by XRD using a Rigaku Miniflex automated powder diffractometer and Cu K α radiation. The scan electron microscope(SEM) study of the samples was performed on JSM-5600LV electron microscope.

The charge/discharge cycling tests were performed using the CR2032 coin-type cell that consisted of a cathode and lithium metal anode separated by a Celgard 2300 porous polypropylene film. For the fabrication of the positive electrode, 20 mg of Li(Ni $_{1/3}$ Mn $_{1/3}$ Co $_{1/3}$)O $_2$ was accurately weighted and mixed with 12 mg of conductive binder (8 mg of teflonized acetylene black and 4 mg of graphite). The mixture was pressed onto a stainless screen and dried at 170 °C for 5 h under vacuum oven. Lithium foil was used as the negative electrode. The electrolyte was 1 mol/L LiPF $_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC, volume ratio of EC to DMC is 1:2). The cells were assembled in a glove box filled with dried argon gas.

3 Results and discussion

Fig.1 shows the XRD pattern of the precursor spray-drying at 350 °C. Because of the short time and low temperature of the spray-drying process, the crystal of precursor powders is hardly formed. There is little Bragg reflection visible in the pattern originating from the precursor except a nickel nitrate hydroxide Ni(NO $_3$) $_2$ ·2Ni(OH) $_2$ and Co $_3$ O $_4$ are illegibly observed. These compositions are associated with a PVA-nitrate interaction by which NO $_3^-$ groups are replaced by OH $^-$ groups and partial hydrolyze and decompose in the precursor.

The TG and DTA curves of the precursor are shown in Fig.2. Because of PVA-nitrate interaction and

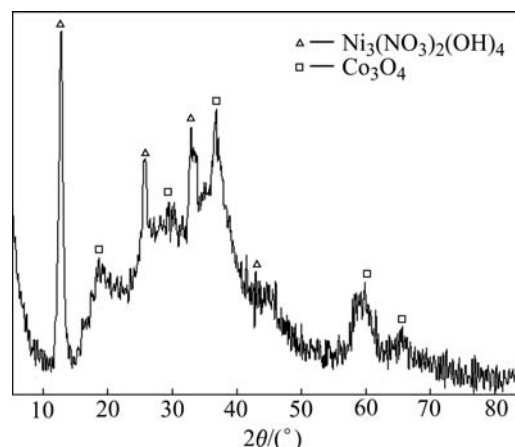


Fig.1 XRD pattern of Li(Ni $_{1/3}$ Mn $_{1/3}$ Co $_{1/3}$)O $_2$ precursor

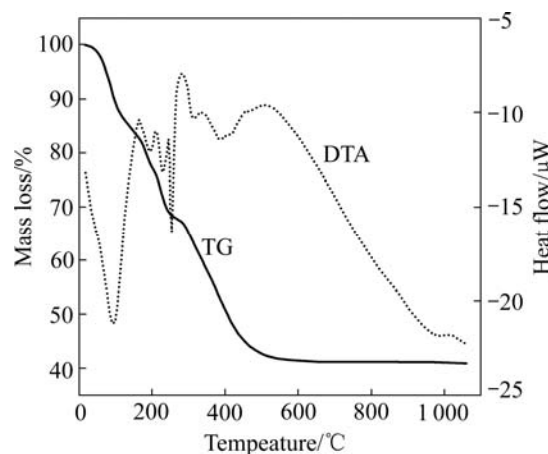


Fig.2 TG and DTA curves of precursor formed by spray-drying method

complex composition, the reaction mechanism during sintering is difficult to be analyzed. The first mass loss in the temperature range below 160 °C on the TG curve is due to the removal of the absorbing and structural water from each chemical component, which is accompanied by a strong endothermic peak. The second mass loss occurs in the temperature region below 240 °C. In the DTA curve, there are two peaks. These peaks are related to the decomposition and synthesis among the mixed precursor. The steeper endothermic peak evidenced by DTA at 250 °C is ascribed to LiNO $_3$ melting. The mass loss of the starting materials is almost terminated at 600 °C, indicating that the organic compounds and chemical component can be removed and the decomposition finished completely at temperatures lower than 600 °C. From the thermal analysis, Li(Ni $_{1/3}$ Mn $_{1/3}$ Co $_{1/3}$)O $_2$ can be obtained at a temperature around 600 °C.

After sintering the precursor at 600, 700, 800, 900 and 1 000 °C for 10 h, the XRD patterns of the compounds Li(Ni $_{1/3}$ Mn $_{1/3}$ Co $_{1/3}$)O $_2$ are shown in Fig.3. The layered Li(Ni $_{1/3}$ Mn $_{1/3}$ Co $_{1/3}$)O $_2$ crystal peaks can be observed from all samples sintered at different tempera-

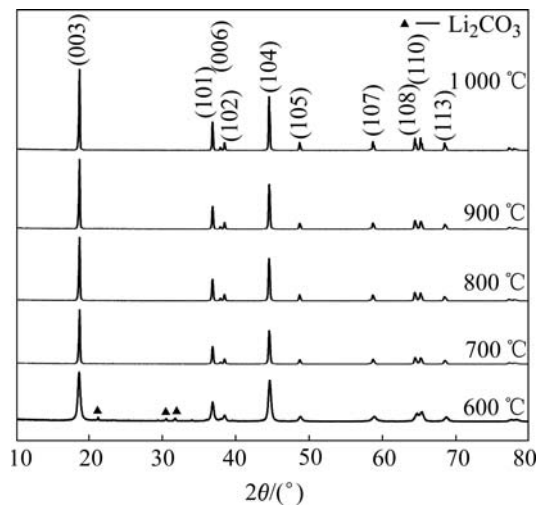


Fig.3 X-ray diffraction patterns of $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ obtained at different temperatures

tures. But many other peaks of Li_2CO_3 are also found in the sample sintered at 600 °C. Li_2CO_3 formation is related to the improved dispersion of Li (or very fine LiNO_3 crystals) in the PVA matrix and the PVA combustion. This phenomenon has already been observed in the $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ synthesis by spray-drying process[17]. The XRD patterns of the powders sintered at 700, 800, 900 and 1 000 °C are $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ similar to that of LiCoO_2 ($\alpha\text{-NaFeO}_2$ type, space group $R\bar{3}m$) and no impure peaks appear. The relative intensities of the diffraction

peaks enhance with increasing sintering temperature. Cation mixing is known to deteriorate the electrochemical performance of the layered compounds. The integrated intensity ratio of the lines (003) to (104) (R) in the XRD patterns is shown to be a measure of the cation mixing and $R < 1.2$ is an indication of undesirable cation mixing[18]. The lattice constants, a and c , c/a ratio, V , and the intensity ratio I_{003}/I_{104} of the hexagonal unit cell are listed in Table 1. With the temperature increased from 600 to 900 °C, the intensity ratio of I_{003} to I_{104} increases from 1.060 1 to 1.214 8. When the materials are calcined at 1 000 °C, this ratio decreases to 1.192 2. The best results come from the materials calcined at 900 °C and show little evidence of ion mixing.

The typical SEM photographs of the precursor and $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ powders sintering at 900 °C are shown in Fig.4. From SEM photographs, the particles of the precursor are spherical with size distribution in the range of 5–20 μm . The surface of every spherical particle is not very smooth with some wrinkles. The morphology of the $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ powders is resulted from the precursor and agglomerated by the crystalline grains to spherical morphology. The spherical powders exhibit higher tap-density and less agglomeration than irregular particles[18], which is important to improve the volume energy of the powders.

The initial charge—discharge curves of $\text{Li}/\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ sintered at different temperatures for 10 h,

Table 1 Lattice parameters of $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ prepared by sintering at different temperatures

Temperature/°C	a/nm	c/nm	c/a	V/nm^3	I_{003}/I_{104}
600	0.285 56	1.424 16	4.987 2	0.100 60	1.060 1
700	0.285 49	1.422 39	4.982 3	0.100 40	1.130 7
800	0.286 08	1.424 47	4.979 3	0.100 90	1.190 3
900	0.285 96	1.423 69	4.978 6	0.100 83	1.214 8
1 000	0.285 88	1.423 61	4.979 7	0.100 76	1.192 2
From Ref.[9]	0.286 70	1.424 60	4.969 0	0.101 40	—

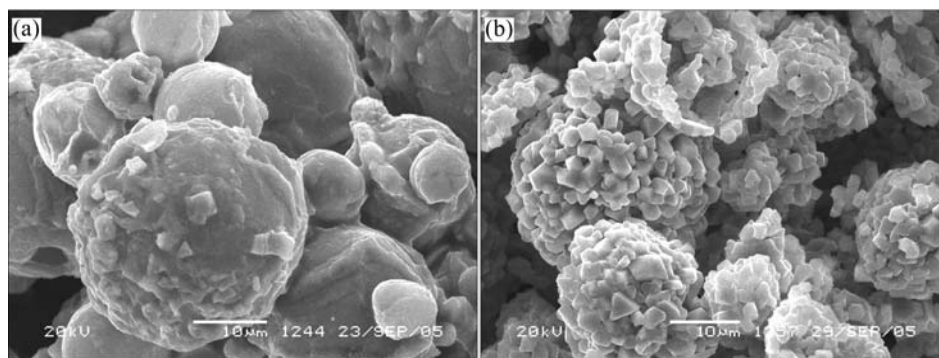


Fig.4 SEM images of precursor and layered $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ powders: (a) Precursor powders; (b) $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ powders sintered at 900 °C

at a discharge rate of $0.2C$ in the potential range from 3.00 to 4.35 V, are shown in Fig.5. The $\text{Li}/\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ cell has a very smooth and monotonous voltage profile, similar to the voltage profiles reported by OHZUKU et al[9] and SHAJU et al[10]. The sintering temperature remarkably affects the electrochemical characteristics of the $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$. The discharge capacities increase linearly with increasing sintering temperature from 600 to 900 °C. As the sample is sintered at 900 °C, the observed discharge capacity is about 153 mA·h/g. This obtained capacity is comparable with that of the reported in Refs.[9,11–12]. However, when the sintering temperature reaches 1 000 °C, the discharge capacity decreases to 145 mA·h/g, which is attributed to the volatilization of lithium at high temperature. Fig.6 shows the cycling behavior of the samples sintered at different temperatures at a discharge rate of $0.2C$. The sample sintered at 900 °C exhibits very stable cyclability with little capacities loss after the 40th cycle. The cycling performance becomes worse at other sintering temperatures.

Figs.7 and 8 show the rate performance of the sample sintered at 900 °C with various current densities

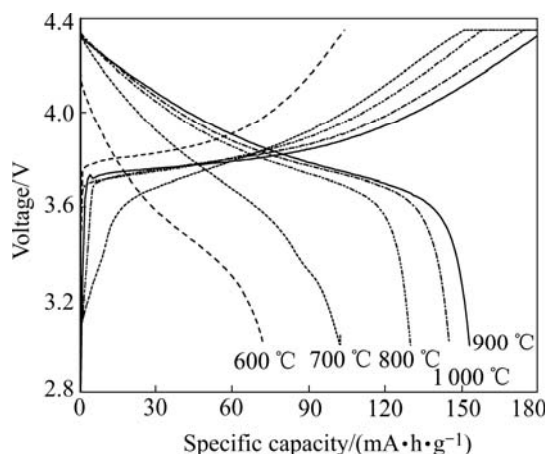


Fig.5 Typical initial charge—discharge curves of $\text{Li}/\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ cells

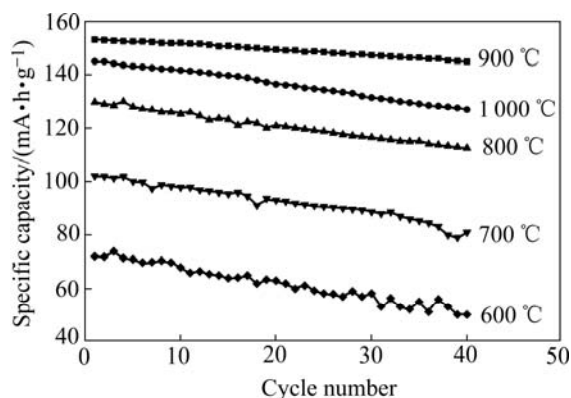


Fig.6 Cycle performance of samples sintered at different temperatures at discharge rate of $0.2C$ on $\text{Li}/\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ cell

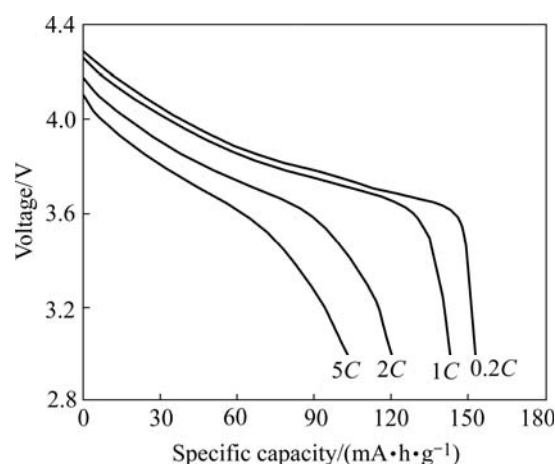


Fig.7 Initial discharge curves of $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ sintered at 900 °C with various current densities

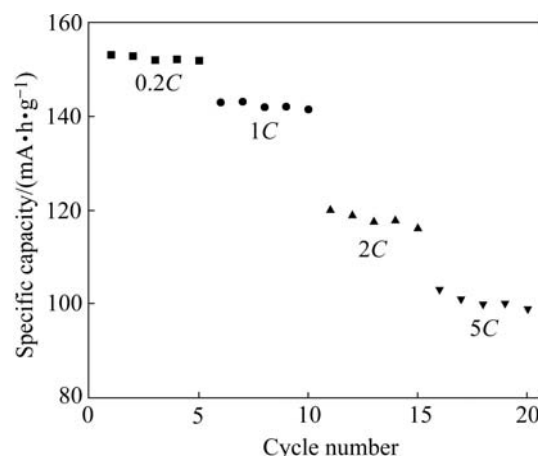


Fig.8 Rate performance of $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ sintered at 900 °C

between potential limits of 3.00–4.35 V. The cell is charged at a current density of 30 mA/g ($0.2C$) before each discharge test. The first discharge capacity of the sample decreases from 153 to 98.9 mA·h/g when the discharge current density increases from 30 mA/g ($0.2C$) to 750 mA/g ($5C$), indicating that only 65% of initial discharge capacity can be retained.

4 Conclusions

1) Layered $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ powders with high homogeneity, spherical morphology and high capacity are synthesized by solution spray-drying method. Li_2CO_3 is detected by XRD when the precursor is prepared at low temperature. The Li_2CO_3 formation is related to the drying conditions of the precursor and the PVA combustion step.

2) The sintering temperature strongly affects the structure and the electrochemical performance. The layered $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ powders synthesized at 900 °C for 10 h exhibit high discharge capacity and good

cycling properties.

3) Spray-drying method is considered to be a promising alternative way to synthesize oxide electrode materials with homogeneous and spherical morphology for lithium-ion secondary batteries.

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(Edited by CHEN Wei-ping)