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# Synthesis and electrochemical performances of high-voltage $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials prepared by hydroxide co-precipitation method

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**Abstract** Spherical cathode material $LiNi_{0.5}Mn_{1.5}O_4$ for lithium-ion batteries was synthesized by hydroxide co-precipitation method. X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical measurements were carried out to characterize prepared $LiNi_{0.5}Mn_{1.5}O_4$ cathode material. SEM images show that the $LiNi_{0.5}Mn_{1.5}O_4$ cathode material is constituted by micro-sized spherical particles (with a diameter of around 8 μm). XRD patterns reveal that the structure of prepared $LiNi_{0.5}Mn_{1.5}O_4$ cathode material belongs to *Fd*3*m* space group. Electrochemical tests at 25 °C show that the $LiNi_{0.5}Mn_{1.5}O_4$ cathode material prepared after annealing at 600 °C has the best electrochemical performances. The initial discharge capacity of prepared cathode material delivers 113.5 $mAh \cdot g^{-1}$ at 1C rate in the range of 3.50–4.95 V, and the sample retains 96.2% (1.0C) of the initial capacity after 50 cycles. Under different rates with a cutoff voltage range of 3.50–4.95 V at 25 °C, the discharge capacities of obtained cathode material can be kept at about 145.0 (0.1C), 126.8 (0.5C), 113.5 (1.0C) and 112.4 $mAh \cdot g^{-1}$ (2.0C), the corresponding initial coulomb efficiencies retain above 95.2% (0.1C), 95.0% (0.5C), 92.5% (1.0C) and 94.8% (2.0C), respectively.

**Keywords** Lithium-ion battery; $LiNi_{0.5}Mn_{1.5}O_4$; Hydroxide co-precipitation; Electrochemical performance

## 1 Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used in portable electronic devices due to their high energy density, high power density and good cycling stability [1–4]. Currently, $LiCoO_2$, $LiNiO_2$, $LiFePO_4$, $LiNi_xCo_yMn_{1-x-y}O_2$ and $LiMn_2O_4$ are the most common cathode materials applied in LIBs [5–7]. Among the numerous transition metal oxides, spinel $LiMn_2O_4$ has been extensively studied as cathode material for its low cost and non-toxicity [8, 9]. The development of hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs) demands for lithium-ion batteries with high power and safety stability, but the traditional $LiMn_2O_4$ material cannot meet the technical requirements. Owing to the dissolution of $Mn^{3+}$ in 4-V discharge platform, the capacity of $LiMn_2O_4$ fades severely during the charge and discharge processes [10–13]. To improve the cycle performance of $LiMn_2O_4$, many researches have focused on the substitution of Mn with other transition metal elements to form new spinel cathode material [14, 15]. Among various doped materials, $LiNi_{0.5}Mn_{1.5}O_4$ cathode material has been seen as one of the most prospective lithium-ion battery materials due to its high theoretical capacity (147 $mAh \cdot g^{-1}$) and high discharge platform [16, 17].

$LiNi_{0.5}Mn_{1.5}O_4$ has been prepared by many methods, including solid-state reaction [18, 19], hydrothermal [20], sol–gel [21, 22] and co-precipitation [23, 24]. Among these methods, the co-precipitation method received extensive attention on account of simplicity in operation and easiness

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in industrialization [25]. Generally, carbonate and oxalate are used as precipitants for preparing $LiNi_{0.5}Mn_{1.5}O_4$ cathode material by co-precipitation method. The method includes two main steps: (1) the carbonate or oxalate precursor preparation and (2) precursors calcination [26–28]. During calcination process, the carbonate and oxalate precursors decomposition and the gases ($CO_2$) releasing from precursors result in loose structure and poor compactness of final material.

Compared with carbonate or oxalate precipitation method, many spherical cathode materials ($LiCoO_2$, $LiNiO_2$, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$) with high tap density, uniform particle size and better thermal stability could be synthesized by hydroxide co-precipitation method [29, 30]. However, the high content of $Mn^{2+}$ and $OH^-$ is easy to form fine hydroxide precipitant nucleation [31], and the pure $LiNi_{0.5}Mn_{1.5}O_4$ cathode material with regular spherical morphology is hard to be prepared by hydroxide co-precipitation method. Meanwhile, the different solubilities of manganese hydroxide and nickel hydroxide are easy to result in different ratios of nickel and manganese or impurity phases in the final product [32].

In this paper, spherical $LiNi_{0.5}Mn_{1.5}O_4$ cathode material was successfully synthesized via co-precipitation method with the help of sodium hydroxide as precipitant and ammonia as complexing agent. The impurity phases in the final material were successfully reduced by annealing process. The prepared pure $LiNi_{0.5}Mn_{1.5}O_4$ cathode material with spherical morphology exhibited good electrochemical properties.

## 2 Experimental

### 2.1 Synthesis

In order to obtain spherical and pure $LiNi_{0.5}Mn_{1.5}O_4$ powders, spherical precursor $Ni_{0.25}Mn_{0.75}(OH)_2$ was firstly synthesized through co-precipitation method. 1 $mol \cdot L^{-1}$ $NH_3 \cdot H_2O$ solution as mother liquor was added into the reactor. 2 $mol \cdot L^{-1}$ $NiSO_4$ and $MnSO_4$ mixed solution (cation ratio of Ni and Mn = 1:3) was fed into a stirred tank reactor. Meanwhile, 4 $mol \cdot L^{-1}$ NaOH and a certain amount of $NH_3 \cdot H_2O$ solution were injected into the reactor under the conditions of 60 °C and pH = 10. The reaction was protected by $N_2$ atmosphere. The obtained hydroxide precursors were first washed with hot deionized water, and then dried in a vacuum oven under 80 °C for 12 h. Finally, the dry precursors were mixed with an excess of $LiOH \cdot H_2O$ (over 5%), and calcined in air at 500 °C for 5 h and then calcined at 900 °C for 15 h in a muffle furnace. To improve crystallinity and reduce impurity phases, annealing experiments were carried out. The obtained materials after calcination on the condition of 900 °C were annealed for 20 h at 500, 600 and 700 °C, respectively.

### 2.2 Characterizations and electrochemical measurements

The crystal structures of prepared particles were measured by X-ray diffractometer (XRD, Rigaku Ru-200, Cu Kα radiation, 40 kV, 100 mA, $\lambda = 0.154056$ nm) with scan rate of 2 $(°) \cdot min^{-1}$ in the range of 10°–80°. The morphology and size of obtained samples were observed by scanning electronic microscopy (SEM, KYKY-EM3900 M). The molar ratios of Ni and Mn of obtained materials were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, VARIAN, VISTA-MAPX CCD). The specific surface area of prepared materials was measured by the specific surface area and porosity analyzer (Micromeritics, Gemini VII 2390).

CR2032 coin-type cells were assembled to examine the electrochemical properties of cathode materials. The cathode electrodes were prepared by 80 wt% of active material, 10 wt% of acetylene black and 10 wt% of polytetra fluoroethylene (PTFE). A Celgard 2400 polypropylene microporous membrane was performed as separator. The electrolyte was composed of 1 $mol \cdot L^{-1}$ $LiPF_6$ mixture of 1:1 (volume ratio) ethylene carbonate (EC) and dimethyl carbonate (DMC). Pure lithium sheets were used as anode electrodes. The cells were assembled in an argon-filled glove box.

Charge–discharge tests were carried out in the voltage range of 3.50–4.95 V with Land-CT2001A instrument. Cyclic voltammetry (CV, scan rate of 0.1 $mV \cdot s^{-1}$ and voltage range of 3.5–4.9 V) curves and electrochemical impedance spectroscopy (EIS, AC amplitude of 5 mV and frequency range of 0.10 MHz–0.01 Hz) were performed on PARSTAT®2273 electrochemical workstation. The cathode electrodes after charge–discharge cycles were dismantled from cells and dissolved in toluene to obtain charged cathode materials.

## 3 Results and discussion

Figure 1 shows SEM images of obtained $Ni_{0.25}Mn_{0.75}(OH)_2$ precursors and $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials. As shown in Fig. 1a, b, the obtained $Ni_{0.25}Mn_{0.75}(OH)_2$ precursors are spherical with the average particle diameter of about 6 μm. It is found that the secondary precursor particles are uniformly dispersed with clear boundaries and smooth surfaces. $LiNi_{0.5}Mn_{1.5}O_4$ materials formed after calcining and annealing at 500, 600 and 700 °C are shown in Fig. 1c–h, respectively. The obtained $LiNi_{0.5}Mn_{1.5}O_4$

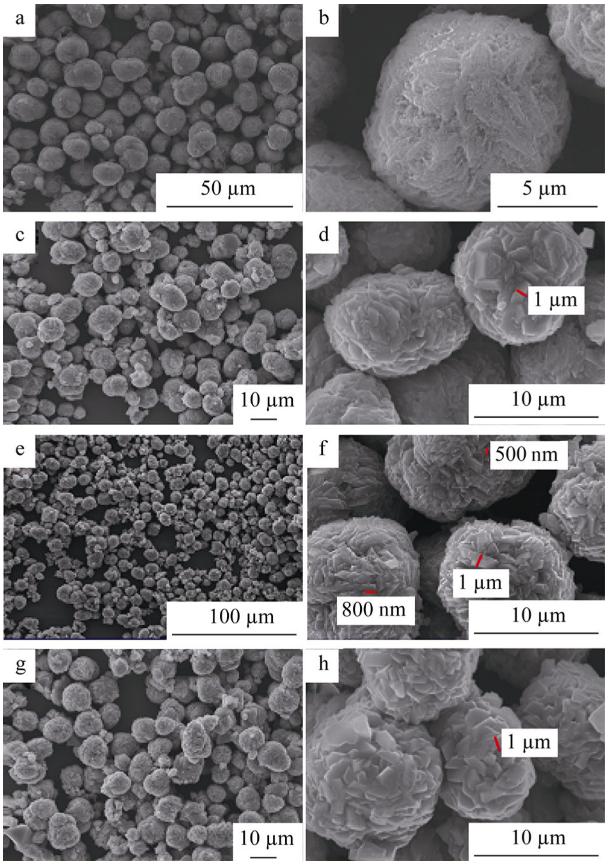

**Fig. 1** SEM images of obtained samples: **a**, **b** $Ni_{0.25}Mn_{0.75}(OH)_2$, **c**, **d** $LiNi_{0.5}Mn_{1.5}O_4$ annealed at 500 °C, **e**, **f** $LiNi_{0.5}Mn_{1.5}O_4$ annealed at 600 °C, and **g**, **h** $LiNi_{0.5}Mn_{1.5}O_4$ annealed at 700 °C

cathode materials inherit the spherical morphology of precursors. The cathode materials $LiNi_{0.5}Mn_{1.5}O_4$ are compact spherical agglomerations and composed of micro- or nano-particles (primary particles). It also can be seen that the boundaries of primary particles of $LiNi_{0.5}Mn_{1.5}O_4$ cathode material are clearer after annealing at 600 °C (Fig. 1f), which means a better crystallization [33]. The pore volumes of cathode materials $LiNi_{0.5}Mn_{1.5}O_4$ after annealing at 500, 600 and 700 °C are $1.01 \times 10^{-2}$, $1.31 \times 10^{-2}$ and $8.04 \times 10^{-3}$ $cm^2 \cdot g^{-1}$, and the corresponding specific surface areas are 8.95, 12.84 and 7.26 $m^2 \cdot g^{-1}$, respectively, which indicates that the cathode material $LiNi_{0.5}Mn_{1.5}O_4$ annealed at 600 °C has the largest specific surface area and can more fully contact with the electrolyte. The molar ratios of Ni and Mn of obtained materials with different annealing temperatures were analyzed by ICP, and the results are listed in Table 1. It can be seen from Table 1 that the molar ratios of Ni and Mn in the final products are similar to the designed contents within the error range. Figure 2 shows XRD patterns of spherical $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials annealed at different temperatures. The structures of $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials prepared by hydroxide co-precipitation method belong to *Fd*3*m* space group, where Mn ions are present as mainly $Mn^{4+}$. In addition, $Li^+$ cations, metal cations ($Mn^{4+}$, $Ni^{2+}$) and $O^{2-}$ anions occupy in the 8a tetrahedral positions, 16d octahedral sites and 32e sites, respectively. For $LiNi_{0.5}Mn_{1.5}O_4$ cathode material without annealing, weak impurity phase $Li_xNi_{1-x}O$ close to peaks of (311) and (400) can be found. According to the paper reported, the impurity $Li_xNi_{1-x}O$ generated for oxygen deficiency has a bad influence on electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_4$ cathode material [23, 34, 35]. To eliminate impurity phases as much as possible, the annealing experiments at different temperatures were carried out. The results shown in Fig. 2 suggest that the impurity peaks reduce and more pure $LiNi_{0.5}Mn_{1.5}O_4$ cathode material can be obtained by annealing process at 600 °C.

**Table 1** Molar ratio results of Ni and Mn obtained by ICP analyses

| Annealing temperature/°C | Molar ratio of Ni and Mn | |
|---|---|---|
| | Designed | Tested |
| 500 | 1:3 | 1.00:3.08 |
| 600 | 1:3 | 1.00:3.06 |
| 700 | 1:3 | 1.00:3.10 |

$LiNi_{0.5}Mn_{1.5}O_4$ cathode materials prepared at different annealing temperatures were monitored by CV curves in Fig. 3. There are common characteristics of a pair of redox peaks in related to 4.55–4.85 V region, which are consistent with the reversible reaction of $Ni^{2+}/Ni^{4+}$. For obtained $LiNi_{0.5}Mn_{1.5}O_4$ materials after annealing at 500 and 700 °C, the slight redox peaks associated with the transformation of $Mn^{3+}/Mn^{4+}$ couple appear in ~4.0 V region. However, the redox peak (4.0 V) of material collected after annealing at 600 °C is weaker. The results corresponding

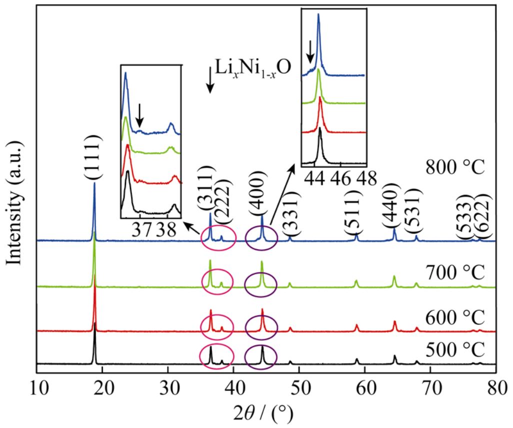

**Fig. 2** XRD patterns of spherical $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials after annealing at different temperatures

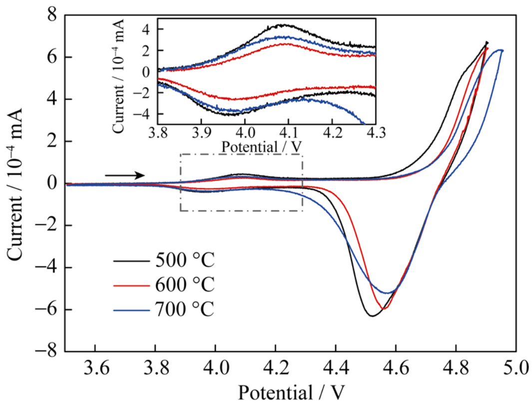

**Fig. 3** CV curves of $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials prepared at different annealing temperatures

to XRD patterns shown in Fig. 2 can further verify that most of $Mn^{3+}$ ions have been reduced by annealing process at 600 °C and more pure $LiNi_{0.5}Mn_{1.5}O_4$ cathode material is obtained. Remarkably, the more pure $LiNi_{0.5}Mn_{1.5}O_4$ may have better electrochemical performances.

Initial charge and discharge capacity and coulomb efficiency of obtained $LiNi_{0.5}Mn_{1.5}O_4$ after annealing at different temperatures with a cutoff voltage range of 3.50–4.95 V at different rates at 25 °C are shown in Table 2. It can be seen from Table 2 that $LiNi_{0.5}Mn_{1.5}O_4$ cathode material obtained after annealing at 600 °C shows better capability than others. The initial discharge capacities of cathode material annealed at 600 °C are 145.0 (0.1C), 126.8 (0.5C), 113.5 (1.0C) and 112.4 $mAh{\cdot}g^{-1}$ (2.0C), and the corresponding coulomb efficiencies maintain 95.2%, 95.0%, 92.5% and 94.8% in the first cycle at a rate of 0.1C, 0.5C, 1.0C and 2.0C, respectively. It verifies that the initial irreversible capacity loss is minor, and $LiNi_{0.5}Mn_{1.5}O_4$ cathode material annealed at 600 °C has high discharge capacity, good rate performance and preferable reversibility.

Figure 4 shows the charge and discharge profiles of $LiNi_{0.5}Mn_{1.5}O_4$ obtained after annealing at different temperatures with a cutoff voltage range of 3.50–4.95 V at 1.0C and 25 °C. It can be seen from Fig. 4 that all of the discharge and charge curves of the cathode materials annealed at 500 °C (Fig. 4a), 600 °C (Fig. 4b) and 700 °C (Fig. 4c) are similar. Common characteristics of a pair of redox peaks in 4.55–4.85 V region can be found in the discharge curves of all the obtained materials, which are consistent with the reversible reaction of $Ni^{2+}/Ni^{4+}$. Meanwhile, the charge and discharge capacities of the cathode materials annealed at 500, 600 and 700 °C decrease with the cycle number increasing. The cathode material annealed at 600 °C shows better cycle performance. After 50 cycles, the capacities of $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials annealed at 500, 600 and 700 °C are 101.4, 109.2 and 97.7 $mAh{\cdot}g^{-1}$, respectively. The capacity retention of the cathode material annealed at 600 °C (96.2%) is higher than that of materials annealed at 500 °C (87.0%) and 700 °C (95.0%). It is also reported that the impurity $Li_xNi_{1-x}O$ can result in a higher residence and have a bad influence on electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials, and the capacity of pure $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials fades more slowly than that of cathode materials with impurity phases [10–13, 23, 34, 35], so the results of electrochemical performance tests agree well with structure analysis (Fig. 2), CV measurement (Fig. 3) and results reported in Refs [10–13, 23, 34, 35]. Figure 5 shows EIS result of prepared

**Table 2** Initial charge and discharge capacity and coulomb efficiency of $LiNi_{0.5}Mn_{1.5}O_4$ obtained after annealing at different temperatures with a cutoff voltage range of 3.50–4.95 V at different rates and 25 °C

| Annealing temperature/°C | Current rate | Charging specific capacity/($mAh{\cdot}g^{-1}$) | Discharging specific capacity/($mAh{\cdot}g^{-1}$) | Initial coulomb efficiency/% |
|---|---|---|---|---|
| 500 | 0.1C | 134.5 | 125.3 | 93.2 |
| | 0.5C | 134.0 | 122.1 | 91.1 |
| | 1.0C | 127.0 | 116.8 | 92.0 |
| | 2.0C | 135.1 | 113.9 | 84.3 |
| 600 | 0.1C | 152.3 | 145.0 | 95.2 |
| | 0.5C | 133.5 | 126.8 | 95.0 |
| | 1.0C | 122.7 | 113.5 | 92.5 |
| | 2.0C | 118.6 | 112.4 | 94.8 |
| 700 | 0.1C | 125.7 | 112.7 | 89.7 |
| | 0.5C | 123.4 | 111.4 | 90.3 |
| | 1.0C | 130.8 | 102.7 | 78.5 |
| | 2.0C | 101.1 | 95.5 | 74.5 |

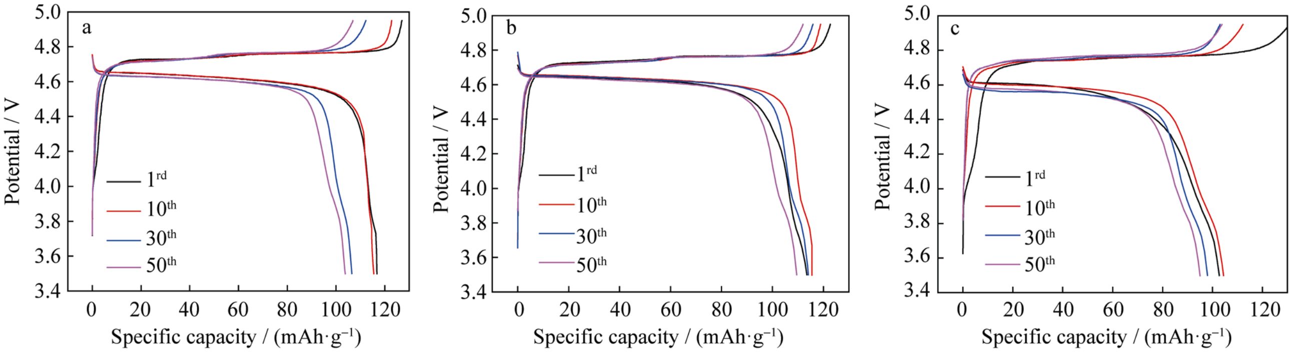

**Fig. 4** Charge and discharge curves of $LiNi_{0.5}Mn_{1.5}O_4$ at 1.0C at annealing temperatures of **a** 500 °C, **b** 600 °C and **c** 700 °C with a cutoff voltage range of 3.50–4.95 V at 25 °C

cathode materials with different annealing temperatures after 50 cycles at 1.0C, where $Z'$ is the real part of impedance and $Z''$ is the imaginary part of impedance. It can be seen from Fig. 5 that EIS of samples consist of a semicircle in the high frequency and a straight sloping line in the low frequency. After 50 cycles at 1.0C, the residence value of the prepared sample annealed at 600 °C is lower than those annealed at 500 and 700 °C, which further indicates that the sample annealed at 600 °C has good ions conductivity and electrochemical performance. Moreover, the prepared $LiNi_{0.5}Mn_{1.5}O_4$ cathode material with best electrochemical performance (annealed at 600 °C) can maintain its morphology during charge–discharge processes. Figure 6 shows SEM image of $LiNi_{0.5}Mn_{1.5}O_4$ annealed at 600 °C after 50 cycles at 1.0C. It can be seen from Fig. 6 that the cathode material keeps the original size and spherical shape, displaying attractive morphological stability. Therefore, the results above indicate that the pure $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials with enhanced electrochemical performance can be prepared via hydroxide co-precipitation method with a suitable controlled annealing temperature.

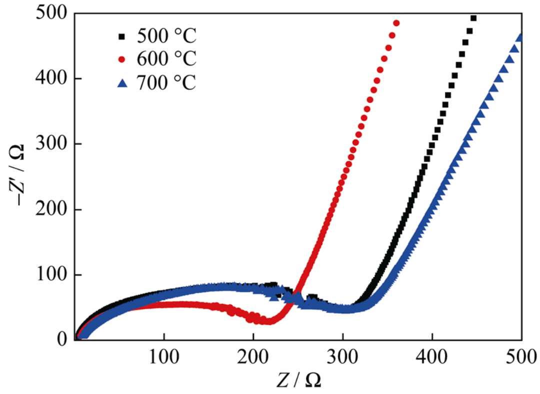

**Fig. 5** EIS results of prepared $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials at different annealing temperatures after 50 cycles at 1.0C

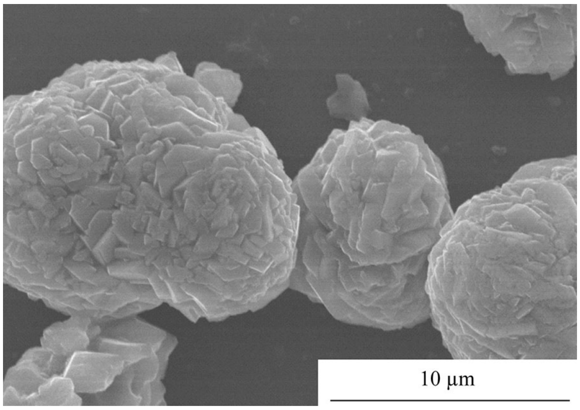

**Fig. 6** SEM image of $LiNi_{0.5}Mn_{1.5}O_4$ annealed at 600 °C after 50 cycles at 1.0C

## 4 Conclusion

In summary, the high-voltage spherical $LiNi_{0.5}Mn_{1.5}O_4$ cathode material for lithium-ion batteries was successfully synthesized by hydroxide co-precipitation method. The prepared $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials are composed of micro- or nano-primary particles. The more pure $LiNi_{0.5}Mn_{1.5}O_4$ cathode material with $Fd3m$ cubic spinel structure and good electrochemical properties can be obtained with the help of an annealing process at 600 °C. For the material prepared under this condition, the initial discharge capacity (0.1C, 145.0 mAh·g$^{-1}$) is close to its theoretical capacity (147 mAh·g$^{-1}$). After 50 cycles, the discharge capacity is 109.2 mAh·g$^{-1}$ at 1.0C with a cutoff voltage range of 3.50–4.95 V at 25 °C and the capacity retention is 96.2%. When the obtained $LiNi_{0.5}Mn_{1.5}O_4$ cathode material discharges under different rates with a cutoff voltage range of 3.50–4.95 V at 25 °C, the discharge capacities are kept at about 145.0 (0.1C), 126.8 (0.5C), 113.5 (1.0C) and 112.4 mAh·g$^{-1}$ (2.0C) and the initial coulomb efficiencies retain above 95.2% (0.1C), 95.0% (0.5C), 92.5% (1.0C) and 94.8% (2.0C), respectively. The results would contribute to performance improvement and industrial production of $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials for 5 V Li-ion batteries.

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