Synthesis of spherical Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$(OH)$_2$ precursor via hydrothermal method assisted by microfluidics

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Abstract: Nickel-rich materials have been considered as promising cathode candidates for Li-ion batteries. In this work, the spherical Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$(OH)$_2$ precursor with good crystalline is synthesized via a hydrothermal method assisted with microfluidics. The effects of (NH$_4$)$_2$CO$_3$ aqueous solution addition ratio and hydrothermal time on the formation of precursors are investigated comprehensively. The as-obtained precursors after optimization (hydrothermal time of 24 h and the concentration of the (NH$_4$)$_2$CO$_3$ is 0.3 mol/L) display the spherical microstructure with homogenously distribution morphology, which can be clearly observed by scanning electron microscope. This work provides a rational route to controllably prepare the spherical Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$(OH)$_2$ precursors.

1. Introduction
In recent years, environment and energy issues have attracted much attention. In order to meet the highly demand for efficient power supply, scientists have made great efforts to develop novel energy storage devices, such as supercapacitors, Li-ion batteries and Na-ion batteries, etc [1]. Among them, Li-ion batteries have been widely investigated due to their high energy density, long cycling stability, operation safety and environmental friendly. To improve the electrochemical performance of Li-ion batteries, researches have devoted to exploring the high efficient electrode materials [1,2]. Ternary materials LiNi$_x$Co$_{y}$Mn$_{1-x-y}$O$_2$ have gained great interest due to their stable microstructure and high charging/discharging capacity [3]. Consequently, it is highly desired to develop a rational route to prepare the cathode material precursors.

Currently, many methods have been reported to synthesis precursors. For example, the solid state method and sol-gel method have both been reported. However, the precursors obtained by these methods are always distributed non-uniformly and the precursor growth is uncontrollable [4,5]. As for co-precipitation method [6], the synthesis conditions of spherical Ni$_x$Co$_y$Mn$_{1-x-y}$(OH)$_2$ must be strictly controlled [7]. Alternatively, the hydrothermal treatment can improve the crystallinity of transition metal oxide cathode materials and the synthesis conditions can be easily controlled. For insistence, Wu et al [8] prepared LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ via the hydrothermal method, the obtained precursors are uniformly distributed but the particle microstructures are irregular. Many studies have reported that the electrochemical performance of the final product greatly depends on the particle size and morphology [9]. The irregular particles form of precursors can decrease the tap density. To overcome this issue,
preparing the precursors with micro-sized spherical particles is an effective way. Therefore, a convenient and controllable method for synthesizing spherical Ni_{x}Co_{y}Mn_{(1-x-y)}(OH)_{2} precursor is necessary.

In this work, we have successfully synthesized spherical Ni_{x}Co_{y}Mn_{(1-x-y)}(OH)_{2} precursor via a hydrothermal method assisted with microfluidics. Firstly, the Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_{2} precursor was synthesized by microfluidics. And then we applied hydrothermal treatment to the precursor. This method could obtain a spherical morphology of the Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_{2} precursor. The synthesis conditions of the spherical Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_{2} precursor were investigated comprehensively.

2. Experimental

The preparation of spherical Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_{2} precursor is shown in Figure 1. Briefly, NiSO_{4}·6H_{2}O, CoSO_{4}·7H_{2}O and MnSO_{4}·H_{2}O were dissolved in deionized water with the mole ratio of 8:1:1. The solution was pumped into the microfluidics. At the same time, the Na_{2}CO_{3} and (NH_{4})_{2}CO_{3} solutions were separately pumped into the microfluidics. Then the suspension was transferred to a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 180 °C under auto-generated pressure for 24 h, followed by cooling to room temperature naturally. Finally, the obtained precipitate was filtered and washed by distilled water for several times, and dried overnight.

The morphological features and particle sizes were observed by scanning electron microscope (SEM, QUANTA 600).

3. Results and discussion

3.1. Effect of hydrothermal treatment on the morphology of materials

The SEM images of the Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_{2} before and after hydrothermal treatment are shown in Figure 2. The morphologies of the as-prepared precursors under two treatment conditions are completely different. The precursors (before hydrothermal treatment, Figure 2a) directly synthesized from the microfluidics were composed of small particles with agglomerate structures. However, after hydrothermal treatment, the precursors (Figure 2b) are uniformly distributed and clearly exhibit a spherical-like morphology constructed with many rock-shaped squares. It can be seen that the particle size is approximately 5 μm. In this case, the original nanoparticles can be uniformly mixed in microfluidics, which is beneficial for precursors growth controllably during hydrothermal treatment.
3.2. Effect of (NH₄)₂CO₃ aqueous solution addition during hydrothermal treatment

To study the effect of (NH₄)₂CO₃ addition amount during hydrothermal treatment, the additional concentration of (NH₄)₂CO₃ aqueous solution in the microfluidics were adjusted to 0.05 mol L⁻¹, 0.1 mol L⁻¹, 0.2 mol L⁻¹ and 0.3 mol L⁻¹, respectively. Figure 3 shows the SEM images of Ni₀.₈Co₀.₁Mn₀.₁(OH)₂ powers obtained from different addition amount of (NH₄)₂CO₃ aqueous solution. It is obviously observed that the amount of (NH₄)₂CO₃ aqueous solution plays an important role in the formation of microstructure and morphology of precursors. It can be concluded that the precursors particles become more compact and spherical as the concentration of NH₄⁺ increased, which could contribute to the cycling stability of cathode materials during charging/discharging process.

Figure 2. SEM images of Ni₀.₈Co₀.₁Mn₀.₁(OH)₂ (a) before hydrothermal treatment and (b) after hydrothermal treatment.

Figure 3. SEM images of Ni₀.₈Co₀.₁Mn₀.₁(OH)₂ powers derived from various concentration of (NH₄)₂CO₃. (a) 0.05 mol L⁻¹, (b) 0.1 mol L⁻¹, (c) 0.2 mol L⁻¹ and (d) 0.3 mol L⁻¹.
3.3. Effect of hydrothermal time on materials formation

The effect of the hydrothermal time on precursors formation was also investigated. In this study, the hydrothermal time was adjusted to 3 h, 9 h, 12 h and 24 h, respectively. The SEM images of particles obtained from different hydrothermal time are shown in Figure 4. It can be seen that the precursor nanoparticles gradually assemble into micro-sized spherical block with the hydrothermal time increased. The corresponding formation route may be according to the following steps: 1) The primary particles directly obtained from the microfluidics begin to dissolve when the hydrothermal time is elongated. 2) The dissolved nucleus accumulates and assembles into spheres after enough time treated.

![Figure 4. SEM images of Ni0.8Co0.1Mn0.1(OH)2 powers derived from different hydrothermal time. (a) 3 h, (b) 6 h, (c) 12 h and (d) 24 h.](image)

4. Conclusions

The controllable and spherical Ni0.8Co0.1Mn0.1(OH)2 precursors were prepared by hydrothermal treatment assisted with microfluidics. The effects of the hydrothermal treatment, the amount of the concentration of (NH4)2CO3 and hydrothermal time on the morphology of precursors were investigated. The hydrothermal treatment for 24 h and the concentration of the (NH4)2CO3 was 0.3 mol L⁻¹, the particles become the spherical and are uniformly distributed. It was concluded that this work provides a promising method for synthesizing spherical Ni0.8Co0.1Mn0.1(OH)2.

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