Investigation of Ph on Electrochemical Performances of Ni-Rich NCM Cathode Material Precursor

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Investigation of Ph on Electrochemical Performances of Ni-Rich NCM Cathode Material Precursor

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Abstract. Ni-rich NCM cathode material is widely recognized as one of the most cathode materials for lithium ion power batteries due to its high specific capacity, high energy density and low cost. In this paper, the NCM cathode material precursor $Ni_{0.8}Co_{0.1}Mn_{0.1}$ $(OH)_2$ was prepared by coprecipitation method and the optimum conditions were explored. Also, the effects of different pH values on the morphology and electrochemical performance of the prepared materials were investigated. The results showed that the best synthesis conditions of the precursor are pH=10. The precursor has a regular morphology and uniform particles. The samples calcined under oxygen atmosphere displays the best electrochemical properties. The initial coulombic efficiency is 85.48% at 0.2 C, the discharge specific capacity is up to 192 mAh·g^{-1} at 0.2 C.

1. Introduction

As the energy crisis becomes more and more serious, the sustainable development of new energy is particularly important. Lithium-ion batteries have become the focus of research in recent years due to their high energy density, long cycle life, good safety performance, low self-discharge efficiency and non-memory effect. Although $LiCoO_2$ is the most widely used cathode material in commercial lithium-ion secondary batteries [1, 2], the resource of cobalt is poor and it is expensive. Therefore, extensive researches have been carried out over the past 10 years to find alternative cathode materials for lithium-ion secondary batteries, in which layer-structured material Li $(Ni_xCo_yMn_z)$ O2 has shown good electrochemical performance and safety characteristic. It is considered to be one of the most possible alternative materials for $LiCoO_2$. Because the α-$NaFeO_2$ layered structure of Li $(Ni_xCo_yMn_z)$ O2 (NCM) combines the excellent properties of each three elements (Ni, Co and Mn) due to its excellent ternary synergistic effect.

In this paper, NCM cathode material precursor is prepared by sulfate coprecipitation method. The effects of pH on the morphology and electrochemical performance of the materials in coprecipitation reaction were investigated. The structure, morphology and electrochemical performance of prepared materials were characterized by different analytical and testing methods.

2. Experimental

$NiSO_4 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, $CoSO_4 \cdot 7H_2O$ were weighed according to the stoichiometric ratio Ni:Co:Mn = 8:1:1 and stirred in deionized water until completely dissolved to configure a 2 mol/L sulfate solution. Then, 2 mol/L $NH_3 \cdot H_2O$ was added into this solution under the continuously stirred reactor. Meanwhile, a hanging bottle was used to control the flow rate of 4mol/L NaOH to ensure the pH=10, pH=10.5, pH=11, pH=11.5 (marked as pH10, pH10.5, pH11, pH11.5, respectively). The water bath temperature was controlled at 60 ℃ during this process. The entire reaction process was carried out under a protection atmosphere of Ar last for 12 h. After the completion of the reaction, maintaining the temperature for a 12 h aging. All products were filtered repeatedly until the filtrate pH=7. Then, the product was placed in a blast oven to obtain an NCM material precursor at the temperature of 80℃ for 12 h. The precursor mixed with $LiOH \cdot H_2O$ and then placed in a tube furnace. Then, temperature was raised to 500 ℃ for 4 h and then temperature raised to 750 ℃ for 15 h. Finally, after cooling to room temperature, NCM cathode material was obtained.

3. Results and discussion
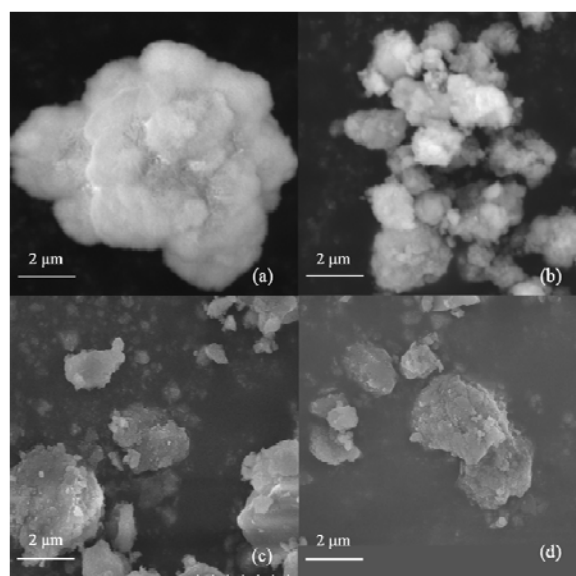
Figure. 1 SEM images of precursor sample (a) pH10, (b) pH10.5, (c) pH11, and (d) pH11.5.

As shown in the Fig.1, it can be clearly to see that the secondary particle size decreases as the reaction pH increases, and then increases. The secondary particles size of sample pH10, pH10.5, pH11 and pH11.5 are 10-12 μm, 5-6 μm, 2-3 μm, 2-4 μm, respectively. And the morphology of the secondary particles from spherical shape gradually became into small spherical shape and finally became into irregular shape with the increasing of pH. Because the secondary particles are composed of primary particles, sample pH10 and pH10.5 could see the small primary particles which are filamentous at the size of 800 nm and 400 nm, respectively. As for other two samples, the primary particles size decreases rapidly because of the increase pH, which results to an irregular shape secondary particle that agglomerated by primary particles.
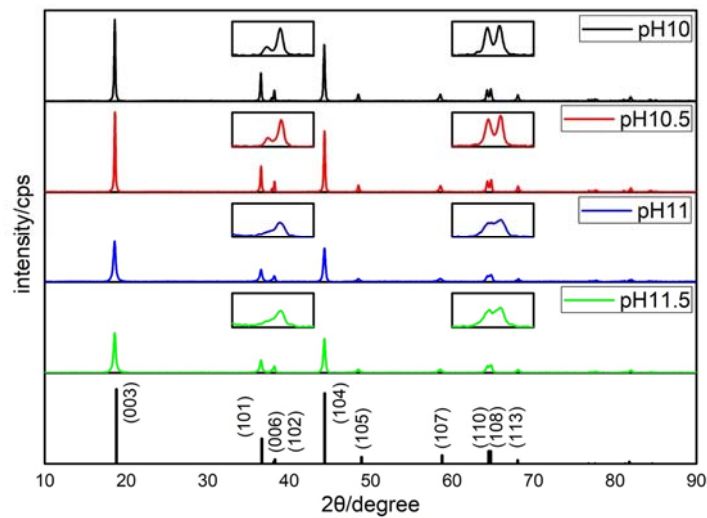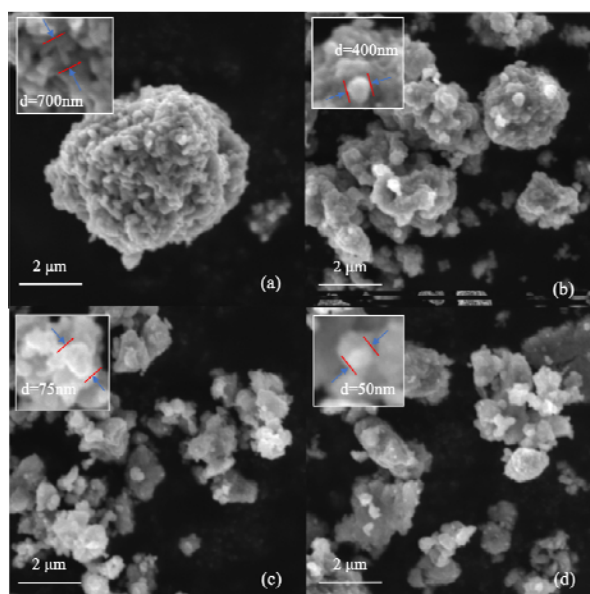
Figure. 2 XRD patterns of sample pH10, pH10.5, pH11, and pH11.5.

As shown in the Fig.2, the XRD peak of the sample is basically the same and no impurity peak appears. The splitting of the (108), (110) and (006), (102) peaks seen in XRD indicate a well-ordered α-NaFeO$_2$ structure which facilitates the insertion and extraction of lithium ions. Besides, the lattice constants a and c calculated from the Jade analysis and XRD data are shown Tab.1 The value of c/3a is an important factor for determining the layered structure, and the larger the value, the better the layered structure, which provides the tunnels for Li-ions diffusion and improve the rate performance of the material [3, 4]. The higher ratio of I$_{(003)}$/I$_{(104)}$, the higher cation ordering, which generally greater than 1.3 and the larger the better [3, 4]. In addition, the value of (I$_{(006)}$+I$_{(102)}$)/I$_{(101)}$ is usually used to judge the order of the hexagonal close-packed structure. It is generally about 0.5, the lower value the better structure.

Table. 1 Lattice Constants and XRD data of sample pH10, pH10.5, pH11, and pH11.5.

Series	a=b (Å)	c (Å)	c/3a	I$_{(003)}$/ I$_{(104)}$	(I$_{(006)}$+I$_{(102)}$) / I$_{(101)}$
pH10	2.87582	14.22255	1.6485	1.4465	0.5145
pH10.5	2.87507	14.21975	1.6486	1.3110	0.5538
pH11	2.87509	14.20750	1.6472	1.1855	(006) not exists
pH11.5	2.87718	14.20262	1.6454	1.1440	(006) not exists

Figure. 3 SEM images of sample (a) pH10, (b) pH10.5, (c) pH11 and (d) pH11.5.

Fig.3 shows a comparison of the SEM images of sample pH10, pH10.5, pH11 and pH11.5. Sample pH10 and pH10.5 have spherical shape secondary particles and short rod-like primary particles. However, because of the sheet-like first particles, sample pH11 and pH11.5 cannot form the regular shape of secondary particles but the scattered irregular secondary particles which affects the electrochemical performance.
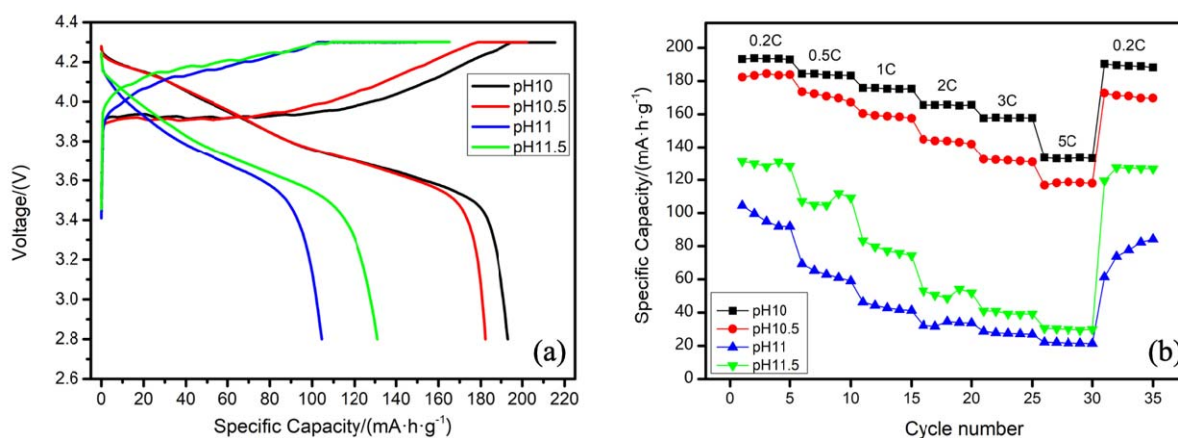
Figure. 4 (a) The initial discharge-charge curves for electrodes at 0.2C between 2.8 V and 4.3 V at 30 ℃. (b) Rate performance of the obtained samples from 0.2C to 5C at 30 ℃.

Sample pH10 has an 85.48% initial efficiency of discharge-charge at 0.2C while sample pH11 only has 70.21%. Besides, sample pH10 also has 192 mA·h·g^{-1} discharge capacity at 0.2C which is almost twice as the sample pH11. Here we can see, there is polarization in electrochemical performance between samples. Due to the data we discussed in Tab.1 before, sample pH10 and pH10.5 have the better layered structure which contributes to their rate performance better than others. Also, the higher cation ordering which results to high capacity retention at the same rate compares to sample pH11 and pH11.5. Besides, the samples with the regular spherical shape secondary particles have the electrochemical performance such as sample pH10 and pH10.5 compare with others. And sample

pH10 has the best performance indicate that the more regular the spherical shape, the better electrochemical performance.

4. Conclusion

In this study, $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ precursors were successfully synthesized by co-precipitation method. The effects of pH on the morphology and electrochemical performance of the materials in coprecipitation reaction were investigated. Due to the changes of the pH, both primary and secondary particles had a huge change in size and morphology. Besides, the lattice constants also showed a significantly effect on electrochemical performance of NCM cathode material. Therefore, the pH=10 is the best synthesis condition of the precursor $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$. After calcination of the material and assembling of the battery, the initial coulombic efficiency is 85.48% at 0.2 C, the discharge specific capacity is up to 192 $mAh \cdot g^{-1}$ at 0.2 C.

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