Effect of calcination time on the electrochemical performance of LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ cathode materials

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Abstract. The layered Ni-rich LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ cathode materials were synthesized by a solid-state method at different calcination times. The structure, morphological and electrochemical performance of the synthesized materials were studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and galvanostatic charge-discharge tests. The results indicate that the sample prepared at 20h delivers higher rate capacities of 184.8, 182.8, 171.2, 158.3, 142.8, and 116.4 mAh g$^{-1}$ at rates of 0.1C, 0.2C, 0.5C, 1C, 2C, and 5C, respectively. And the sample prepared at 16h exhibits better cycle stability than others.

1. Introduction

Lithium ion batteries play an important role in the storage of electric energy, and have been widely used in various portable electronic devices, including electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1-2]. As one of the cathode materials, layered LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ exhibits more superiorities for use in EVs and HEVs because of its low raw material cost, high capacity, better cycling stability, and reliable safety performance [3-4]. LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811), one of the LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ materials system, displays a promising commercial applications due to its high reversible capacity (200 mAh g$^{-1}$). However, NCM811 exhibits some inherent shortages, such as the inherent structural instability, residual lithium on the surface of particles, and the dissolution of transition metals into electrolyte. In order to overcome the above drawback of NCM811, extensive methods have been adopted to enhance the electrochemical performance and thermal stability of NCM811 cathode materials. Significant efforts include lattice doping, surface coating/modification, and optimizing synthetic conditions, such as co-precipitation pH value, calcination temperature and heating/cooling rates. Synthetic conditions are considered as important factors in influencing the electrochemical performance of NCM811 cathode materials. Although the effects of lithium content, calcination temperature, and calcination atmosphere have been investigated, the calcination time have not been studied about NCM811 cathode materials.

In this paper, we prepared the NCM811 cathode materials at different calcination times, and investigated the effect of calcination time on crystal structure, surface morphologies, and electrochemical performance of NCM811 cathode materials.

2. Material and Methods

2.1 Synthesis and Characterization

The NCM811 cathode materials were synthesized by a solid-state method. The commercial Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O(OH)$_2$ precursor and stoichiometric LiOH·H$_2$O (excess of 5 mol %) were mixed by ball-milling. Then, the mixture was first calcined at 480 °C for 5 h, and then calcined at 750 °C in oxygen
flow for 12 h, 16 h, and 20 h, respectively. The obtained NCM811 cathode materials were denoted as NCM811-12, NCM811-16, and NCM811-20, respectively.

The powder X-ray diffraction (XRD, Ultima IV, Rigaku) was carried out to analysis the crystal structures of all samples with Cu Kα radiation. The XRD data were obtained at a scanning rate of 0.02° per 10 s in the range of 10°–90°. The SEM (Hitachi SU8020, Japan) was used to observe the morphology of the samples.

2.2 Electrochemical measurements

The electrochemical performance of all samples were studied in coin-type CR2032 cells, which were assembled in an argon-filled glovebox. To prepare the cathode slurry, the samples super-P, and polyvinylidene fluoride (PVDF) were mixed in a mass ratio of 80:10:10, dispersing in the N-methyl-2-pyrrolidone (NMP) solvent. Then, the positive electrodes with a diameter of 12 mm were obtained after a series of processes of coating on aluminium foil, drying at 105°C in vacuum, and punching into disks. In the cells, there are four main devices, including the as-prepared positive electrodes, the Celgard 2400 (Celgard Inc., USA) as separator, the 1 mol L\(^{-1}\) LiPF\(_6\) in EC/EMC/DC as electrolyte solution, and the Li foil as negative electrodes.

The rate capacities and cyclic performance tests of samples were performed under various C-rates of 0.1C, 0.2C, 0.5C, 1C, 2C, and 5C (the current density at 1C is 200 mA g\(^{-1}\)) between 2.8 V and 4.3 V with galvanostatic charge-discharge units (Land 2001A, Wuhan, China).

3. Result and Discussion

3.1 Material Characterization

Figure 1 presents the XRD patterns of all samples calcined at different times ranging from 12 to 20 h. The XRD diffraction peaks of all samples are indexed to the hexagonal \(\alpha\)-NaFeO\(_2\) structure with R-3m space group. The clear splitting peaks of the (006)/(102) and (108)/(110) of all samples demonstrates that all samples have a well-developed layered structure [5], which indicates that calcination time does not have obvious influence on the layered structure of NCM811 materials. The full width at half maximum (FWHM) of (003) XRD peaks are 0.134, 0.137 and 0.171 for NCM811-12, NCM811-16, and NCM811-20, respectively, which increases with increase of calcination time, revealing a decrease of crystallite size in the synthesized materials. The intensity ratio of (003) and (104) diffraction peaks are 1.45, 1.38 and 1.27 for NCM811-12, NCM811-16, and NCM811-20, respectively, which indicates that cation mixing of Li\(^{+}\)/Ni\(^{2+}\) increases with extension of calcination times.

![Figure 1. XRD patterns of all samples](image-url)

The morphology of all samples examined by SEM was shown in Figure 2. All the samples exhibit a rough surface morphology with tiny particles on the borders of particles, which could be the synthetic residues of LiOH/Li\(_2\)CO\(_3\). Moreover, although the samples are calcined at different times, the clear difference in the size of primary particles among the samples is not be found, which is about 100–300 nm.
3.2 Electrochemical properties

Figure 3 exhibits the rate capacities curves of all samples at different C-rates. As shown in the Figure 3, the discharge capacities of all samples are close to each other at low rates from 0.1C to 0.5C. However, the NCM811-16 and NCM811-20 samples exhibit better high rate capacities than NCM811-16 sample. Moreover, when the rate return to 0.2C after cycled, the NCM811-20 sample exhibits highest discharge capacity (180.2 mAh·g⁻¹), suggesting better structural stability of the NCM811-20 sample.

Figure 4 displays the cycling performance curves of all samples at 0.5C rate. As shown in the Figure 4, the NCM811-20 sample exhibits highest cycling capacities before the 70 cycles. However, the cycling capacities of NCM811-12 and NCM811-20 samples rapidly decreased with the increase of cycles, and the NCM811-20 sample exhibits lower rate of capacity degradation. The NCM811-20 sample exhibits a higher capability of 109.5 mAh·g⁻¹ than those of NCM811-12 and NCM811-20 samples, and the cyclic capacity retention of NCM811-20 sample is 64.0%.

4. Conclusion

In this work, the nickel-rich layered LiNi₀.₈Co₀.₁Mn₀.₁O₂ cathode materials were prepared successfully by a solid-state method at different calcination times. The characterization results show that all samples show the hexagonal structure of α-NaFeO₂. The electrochemical results indicate that the sample prepared at 20h delivers higher rate capacities, and the sample prepared at 16h exhibits better cycle stability than others.

Acknowledgments

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