Synthesis and electrochemical properties of Li[Ni$_x$Co$_y$Mn$_{1-x-y}$]O$_2$ (x, y = 2/8, 3/8) cathode materials for lithium ion batteries

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Abstract

The uniform layered Li(Ni$_{2/8}$Co$_{3/8}$Mn$_{3/8}$)O$_2$, Li(Ni$_{3/8}$Co$_{2/8}$Mn$_{3/8}$)O$_2$, and Li(Ni$_{3/8}$Co$_{3/8}$Mn$_{2/8}$)O$_2$ cathode materials for lithium ion batteries were prepared using the hydroxide co-precipitation method. The effects of calcination temperature and transition metal contents on the structure and electrochemical properties of the Li-Ni-Co-Mn-O were systemically studied. The results of XRD and electrochemical performance measurement show that the ideal preparation conditions were to prepare the Li(Ni$_{3/8}$Co$_{3/8}$Mn$_{2/8}$)O$_2$ cathode material calcined at 900°C for 10 h. The well-ordered Li(Ni$_{3/8}$Co$_{3/8}$Mn$_{2/8}$)O$_2$ synthesized under the optimal conditions has the $I_{003}/I_{104}$ ratio of 1.25 and the $R$ value of 0.48 and delivers the initial discharge capacity of 172.9 mA·h·g$^{-1}$, the discharge capacity of 166.2 mA·h·g$^{-1}$ after 20 cycles at 0.2C rate, and the impedance of 558 Ω after the first cycle. The decrease of Ni content results in the decrease of discharge capacity and the bad cycling performance of the Li-Ni-Co-Mn-O cathode materials, but the decreases of Mn content and Co content to a certain extent can improve the electrochemical properties of the Li-Ni-Co-Mn-O cathode materials.

Keywords: lithium ion batteries; cathode material; electrochemical properties; hydroxide co-precipitation method

1. Introduction

LiCoO$_2$ is the most widely used positive material in commercial secondary batteries, as it is easy to prepare and has good recharge ability even at high rate performances. However, the toxicity and high cost of cobalt represent some of the problems of this material. Thus, extensive research has been carried out to find alternative positive electrode materials such as LiFePO$_4$ [1-2] and LiMn$_2$O$_4$ [3-4].

The layer-structure Li-Ni-Co-Mn-O compound has been considered as a promising candidate of next-generation cathode materials to replace LiCoO$_2$ for rechargeable lithium ion batteries owing to its large capacity and stable structure [5-11, 12]. The layered Li-Ni-Co-Mn-O material can be synthesized with various methods such as hydroxide co-precipitation route [5, 9, 13], carbonate co-precipitation route [14-15], oxalate co-precipitation route [16-17], and all solid state method [18]. The structure stability and cycling performance of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ can be improved by doping or substituting various ions such as Cr [19], Al [20-21], and F [17, 20]. However, the preparation of homogenous Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ is not easy. Selecting a suitable preparation route is important to obtain phase-pure final products. In this study, Li[Ni$_x$Co$_y$Mn$_{1-x-y}$]O$_2$ (x, y = 2/8, 3/8) was synthesized by mixing co-precipitation metal hydroxide, (Ni$_x$Co$_y$Mn$_{1-x-y}$)(OH)$_2$, with 8% excess LiOH·H$_2$O. The influence of calcination temperature on the structure of Li[Ni$_x$Co$_y$Mn$_{1-x-y}$]O$_2$ was studied in detail.

2. Experimental

To prepare a homogenous (Ni$_x$Co$_y$Mn$_{1-x-y}$)(OH)$_2$ (x, y = 2/8, 3/8) precursor, the hydroxide co-precipitation method [6] was applied. An aqueous solution of NiSO$_4$·6H$_2$O, CoSO$_4$·7H$_2$O, and MnSO$_4$·H$_2$O (cations ration of Ni/Co/Mn = x:y:(1-x-y)) with a concentration of 2 mol·L$^{-1}$ was precipitated by adding NaOH solution (aq.) of 2 mol·L$^{-1}$ and a desired amount of NH$_3$·H$_2$O solution (aq.) separately under argon atmosphere along with continued stirring. The solution was maintained at 60°C for 12 h and the pH was controlled to 11-12. Then, the spherical precursor was filtered, washed, and dried in a vacuum at 100°C for 12 h. The transition metal compositions of the precursors were determined by atomic absorption spectroscopy (AAS). The obtained precursor powder was mixed with 8 mol.% excess LiOH·H$_2$O according to the stoichiometric Li, Ni, Co, and
Mn elements (excess amount of Li salts was used to compensate for possible Li loss during the calcinations) thoroughly using a ball mill. The mixture was initially heated to 480°C for 5 h and then calcined at 800 to 950°C for 10 h in air to obtain Li[Ni,Cr−y,Mn1−y]O2. Powder X-ray diffraction was carried out using a Cu Kα radiation of Rigaku D/max 2550 diffractometer.

The cathode was prepared by mixing the active material with carbon back and polyvinylidene fluoride (PVDF) in a mass ratio of 90.5:3.5:6.0. The R2025 cells consisting of the cathode, the lithium foil as an anode, and the electrolyte of 1 mol·L−1 LiPF6 ethylene carbonate (EC)-dimethylene carbonate (DMC)-ethylmethyl carbonate (EMC) (1:1:1 in mass ratio) were assembled in an argon-filled glove box. Cycle tests were performed on the cells between 2.8 and 4.5 V at 16 mA·g−1 at 25°C with a BK6061 testing system (160 mA·g−1 was assumed to be 1C rate).

3. Results and discussion

3.1. Powder characteristics

The obtained brown colored powder from the hydroxide co-precipitation process was used as precursor; the Ni/Co/Mn ratios in the precursor were determined to 2:3:3, 3:2:3, and 3:3:2 by atomic absorption spectroscopy, which are the same as the design value. Fig. 1 shows the powder X-ray diffraction patterns of the Li(Ni2/3Co3/8Mn3/8)O2, Li(Ni3/8Co2/8Mn3/8)O2, and Li(Ni3/8Co3/8Mn2/8)O2 powders synthesized at various temperatures for 10 h. All samples can be indexed to the hexagonal α-NaFeO2 structure (space group R3m). As seen in Fig. 1, the splits in the (006)/(102) and (108)/(110) doublets were observed in all the XRD patterns, which reveals that the layered Li(Ni2/3Co3/8Mn3/8)O2, Li(Ni3/8Co2/8Mn3/8)O2, and Li(Ni3/8Co3/8Mn2/8)O2 cathode materials have been successfully synthesized at all calcination temperatures in this experiment. However, the Li(Ni3/8Co3/8Mn2/8)O2 sample synthesized at 950°C for 10 h has an impurity peak at 2θ = 34.2°.

The structural parameters calculated based on the XRD results for the Li(Ni2/3Co3/8Mn3/8)O2, Li(Ni3/8Co2/8Mn3/8)O2, and Li(Ni3/8Co3/8Mn2/8)O2 powders are summarized in Table 1. Some researchers [22] used the high integrated intensity ratio of the I003/I104 to indicate the cation mixing of the layered structure. Generally, when I003/I104 > 1.2, the cation mixing is small with good layered structure. The I003/I104 values of all the samples in this study are larger than 1.2 except the Li(Ni3/8Co3/8Mn2/8)O2 sample synthesized at 950°C for 10 h, which indicates that no undesirable cation mixing occurred. The I003/I104 values of Li(Ni3/8Co3/8Mn3/8)O2, Li(Ni3/8Co2/8Mn3/8)O2, and Li(Ni3/8Co3/8Mn2/8)O2 powder increase with a decrease in calcination temperature. In addition, Dahn et al. [23] believed that the R factor (R = I102/I006/I104) was an indictor of hexagonal ordering; the lower the R value, the better is the hexagonal ordering. The values of R factor of Li(Ni3/8Co3/8Mn3/8)O2, Li(Ni3/8Co2/8Mn3/8)O2, and Li(Ni3/8Co3/8Mn2/8)O2 samples synthesized at 900°C for 10 h are 0.39, 0.43, and 0.48, respectively, which is lower than those of the samples synthesized at 800, 850, and 950°C, and indicates better hexagonal ordering.

3.2. Electrochemical characteristics for the initial charge-discharge cycle

To further study the influence of calcination temperature on the electrochemical performance of Li[Ni1/3Co1/3Mn1/3]O2, Li[Ni3/8Co2/8Mn3/8]O2, and Li[Ni3/8Co3/8Mn2/8]O2 samples, the test cells were operated at 0.1C rate between 2.8 and 4.5