Effects of Precursor Preparation Methods on the Electrical Properties of Cathode Materials for Lithium Ion Batteries

Yong-di ZHAO¹, Xing ZOU² and Shuai LIU³

University of Science and Technology Beijing, Beijing, 100083, China

*Corresponding author

Keywords: Hydroxide, Carbonate, Co-precipitation, LiNi¹/³Mn¹/³Co¹/³O₂, Electrical properties.

Abstract. Four kinds of precursor powders were synthesized from hydroxide co-precipitation and carbonate co-precipitation methods, then the LiNi¹/³Mn¹/³Co¹/³O₂ was prepared by high temperature calcination, and the precipitating agents were sodium bicarbonate, sodium hydroxide (forward and reverse), sodium hydroxide and ammonia. The effects of precursor preparation methods on the electrical properties of cathode materials for lithium ion batteries were systematically investigated by means of X ray diffraction, scanning electron microscopy and electrochemical performance measurements. The results showed that the LiNi¹/³Mn¹/³Co¹/³O₂ particles obtained by carbonate co-precipitation method were spherical, and the morphology of the precipitated product was similar to that obtained by sodium hydroxide and ammonia. In the voltage range of 3–4.3 V, the delivered discharge capacities of 1-1, 1-2, 1-3 and 1-4 at 1C were 147.0, 145.8, 140.2, 138.1 mAh g⁻¹, respectively. After 50 cycles, the capacity retention ratios were 92%, 89.9%, 85.2%, and 82.1%, respectively.

Introduction

The development of electric vehicles has become the consensus and main task of the automotive industry in the world. The key components of electric vehicles are power batteries, and the technical level is very significant to the popularization and application of electric vehicles. At present, there are three concentrated areas in the world, which are located in Germany, the United States and East Asia. With the expansion of the product capacity of power batteries, power battery showed a rapid decline trend in price. Energy saving and new energy vehicle planning (2012-2020) issued by the State Council focus on the industrialization of power batteries and the standardization of battery modules. It has set up a new energy research and development projects (2016-2020) to support the development of high-performance power batteries in the Thirteenth National five-year plan. The cathode material in the power battery accounts for about 40% of the cost of the battery. Therefore, the development of cheap and high performance cathode materials has been the focus of the research. Due to stable cycling performances, wide working temperature range, high capacity, LiNi¹/³Mn¹/³Co¹/³O₂ is considered to be one of the best candidates of positive electrode materials for hybrid electric vehicle (HEV) power source system [1]. Lee and his cowokers[2] used MnSO₄·H₂O, NiSO₄·6H₂O, CoSO₄·7H₂O and Na₂CO₃ as the starting materials and NH₄OH as a chelating agent, then mixed with LiOH, cathode material LiNi¹/³Mn¹/³Co¹/³O₂ layered structure obtained by high temperature calcination. The first discharge was up to 177mAh/g. Hu and his cowokers[3]used a similar method, the first discharge capacity was up to 181.5mAh/g. The spherical LiNi¹/³Mn¹/³Co¹/³O₂ cathode material was prepared by the carbonate coprecipitation method, the XRD showed that the material had a good layer structure, and the best performance at 800 [4]. KuiYin Hu and his cowokers [5] used MnSO₄·H₂O, NiSO₄·6H₂O, CoSO₄·7H₂O and NH₄HCO₃, NH₃H₂O as the starting materials, the obtained spherical Ni¹/³Co¹/³Mn¹/³(OH)₂ powder was mixed with LiOH·H₂O thoroughly, then layered LiNi¹/³Mn¹/³Co¹/³O₂ materials were prepared by calcination, its discharge capacity was about 169 mAh g⁻¹. So far, no systematic comparison of the properties of LiNi¹/³Mn¹/³Co¹/³O₂ prepared by co precipitation of hydroxide and carbonate has been reported.
Experimental

Preparation of NCM111 Battery

Mixed solution of nickel, cobalt and manganese | NaOH (forward) | NaOH (reverse) | NaOH+NH₄OH | NaHCO₃

↓

Reaction
↓

Filter
↓

Washing
↓

Drying

LiNi₀.₅Mn₀.₅Co₃(OH)₂

Figure 1. LiNi₀.₅Mn₀.₅Co₃(OH)₂ prepared by different methods.

Figure 1 shows the process of preparing Ni₃Mn₀.₅Co₃(OH)₂ and (Ni₃Mn₀.₅Co₁.₅)CO₃ with four methods. The obtained spherical Ni₃Mn₀.₅Co₃(OH)₂ and (Ni₃Mn₀.₅Co₁.₅)CO₃ were dried at 100 °C to remove adsorbed water and mixed with Li₂CO₃ powder thoroughly. The mixture was preheated at 500°C for 5h and then calcined at 900°C for 12 h in air to obtain LiNi₃Mn₀.₅Co₁.₅O₂. The cathode material, the conductive agent (acetylene black) and the PTFE emulsion were uniformly mixed according to the mass ratio of 85:10:5 accurately, and dried in an oven for 24h at 110°C. The mixture was pressed into 0.1mm thick slice with 5~10 mg weight, and then it was rushed into a wafer with a φ8 punch, the positive films were obtained. The lithium tablets were used as anode materials and 1.0 M commercial LiPF₆ in DMC:EC:DEC (1:1:1 by volume) as the electrolyte. The CR2032 button-type batteries were assembled in an argon-filled glove-box.

Characterization and Electrochemical Measurements

The crystal structure of the materials was analyzed by an X-ray diffraction operated at 40 kV and 150 mA from 10° to 90° (Rigaku, D/Max-RB, Japan) with a wavelength of Cu Kα (λ =0.15406nm). Scanning electron microscopy (SEM) was obtained through a spectrometer (SEM, Hitachi S-3400N Japan). Electrical performance test was carried out using a NEWARE tester, Charge-discharge cycles were carried out at 1 C in CR2023 coin cells, with a potential range between 3.0 and 4.3V at room temperature.

Results and Discussion

In order to facilitate the expression, the four methods of respective addition of NaHCO₃, NaOH and ammonia, NaOH (forward), NaOH (reverse) were recorded as 1-1, 1-2, 1-3, 1-4. Figure 2 showed SEM images of the (Ni₃Mn₀.₅Co₁.₅)(OH)₂, (Ni₃Mn₀.₅Co₁.₅)CO₃ and LiNi₃Mn₀.₅Co₁.₅O₂ powders. The precursors prepared by 1-1 showed spherical, smooth and dense. The precursor particles prepared by 1-2 also exhibited spherical shape, but the spherical shape was slightly worse than 1-1, and the morphology of the precipitated product was similar. When sodium hydroxide was used as a precipitant, the particles were randomly distributed and smaller in diameter. The thermodynamics data revealed that the kₚ (solubility product constants) were 1.8×10⁻¹¹ for MnCO₃, 6.6×10⁻⁹ for NiCO₃, and 1.4×10⁻¹³ for CoCO₃, and 2.06×10⁻¹³ for Mn(OH)₂, 2.0×10⁻¹⁵ for Ni(OH)₂, 1.58×10⁻¹⁵
for Co(OH)$_2$ at 25°C. Comparing with the carbonate co-precipitation method, the solubility product constant of hydroxides were much smaller. The characteristics of this kind of compounds in the precipitation synthesis was that the nucleation rate was very fast, and the nucleation rate is much higher than the growth rate of the nucleus, and the morphology was difficult to control and easy to form colloidal precipitate. Ammonia was used as complex of metal ions to reduce the concentration of metal ions and super saturation, reduce the nucleation rate, control the size of the precursor particles and increase the Gibbs free energy required by precipitation, which made the three metal ions co-deposition.

Figure 2. (Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$) (OH)$_2$ and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ SEM diagrams.

Figure 2 shows SEM images of (Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)(OH)$_2$ powders of 1-1 and 1-2, which are spherical particles and composed of many primary particles. The large particles were composed of a sheet-like structure material, and the specific surface area was relatively large, and the precursor of 1-4 was slightly larger particles. The SEM images of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ powders of 1-3 and 1-4 were out of order, in which some spherical secondary particles in 1-3 existed and the particle diameter of 1-4 were distribution small.

Figure 3 and Figure 4 show the electrochemical performance of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cathode materials prepared by four precursors. In the voltage range of 3–4.3 V, the delivered discharge capacities of 1-1, 1-2, 1-3 and 1-4 at 1C were 147.0, 145.8, 140.2, 138.1 mAh/g$^1$, respectively. After 50 cycles, the capacity retention ratios were 92%, 89.9%, 85.2%, and 82.1%, respectively. The crystal structure of the material was complete and the particle diameter was superior, which was beneficial to the deintercalation of lithium ions, reducing the resistance of lithium ion diffusion and increasing the electrochemical performance of the material. The particle size was too large, crystal diffusion speed was slow in charge and discharge of ions, and not conducive to the full infiltration of electrolyte particles coalescence, increasing the lithium ion diffusion resistance and the polarization of the battery, which caused the electrochemical performance of the lithium ion battery to deteriorate.

Figure 3. The first charge and discharge curves of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ synthesized by different methods.
The electrical properties of LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 prepared by 1-1 and 1-2 were better than those of 1-3 and 1-4. Figure 5 was the LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 XRD patterns prepared by methods 1-1 and 1-2, and the products were α-NaFeO_2 layered structures. In the XRD pattern, the diffraction intensities I_{003}/I_{004} and (I_{006}+I_{012})/I_{101} were known to an indicator of characteristic of layered structure like LiCoO_2 and LiNiO_2. The greater the I_{003}/I_{004} ratio, the smaller the (I_{006}+I_{012}) /I_{101} ratio, Ni, Co and Mn occupy a small number of 3b bits in the Li layer [6,7]. Figure 5 showed the diffraction characteristic peaks of the materials which are completely divided, I_{003}/I_{004} was calculated as 1.77,1.70, all were more than 1.2, and (I_{006}+I_{012}) /I_{101} was 0.434 , 0.431 respectively, indicating that the synthesized LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 has a complete layered structure and high crystallinity.

Conclusions

(1) The precursor particles of 1-1 were spherical and the surface was smooth. The surface of precursor particles prepared by 1-2 was rough and the particle consistency was slightly worse, and the morphology of 1-2 was similar to 1-1. The synthesized LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 had a complete layered structure with high crystallinity.

(2) The first charge and discharge capacity of 1-1 was the highest in all methods, and the capacity retention rate was high after 50 cycles, but the difference between 1-1 and 1-2 was not obvious. The detection results of the electrical performance and the quality of precursor were consistent, indicating it is great significant to prepare the precursor of good performance for the LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2.

References


