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Original Research Paper

Synthesis and characterization of manganese-rich transition metal carbonate precursor in the presence of ethanol

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ABSTRACT

Manganese-rich transition metal carbonate precursors ($Ni_{0.15}Co_{0.15}Mn_{0.7}CO_3$) have been synthesized by the carbonate precipitation in the presence of ethanol. The physical properties of the precursors with different concentration of ethanol have been examined by XRD and SEM. The XRD results show that the precursors prepared by this method are typical hexagonal structure. The SEM results show that the particles of the precursors with the presence of ethanol display more spherical and dispersed than those prepared without using ethanol. Galvanostatic charge–discharge experiments demonstrate that the initial discharge capacity of the cathode material ($Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$) is improved by the addition of ethanol. In addition, the effects of reaction temperature, the molar ratio of precipitant/total-cations on the morphology of the resultant precursors and the electrochemical properties of the prepared powders are also investigated. Among the synthesized materials, the sample prepared with 10 vol% ethanol and a fixed concentration ratio ($[CO_3^{2-}]/[M^{2+}] = 10$) at 65 °C exhibits not only a relatively high discharge capacity of 272.1 mA h g^{-1}, but also excellent rate performance and good cycling performance.

1. Introduction

Lithium ion batteries have become the predominant power sources for consumer electronic devices [1–5]. In recent years, a novel type of composite lithium- and manganese-rich $Li_{1+x}M_{1-x}O_2$ (M = Mn, Ni, Co) compounds, denoted in "layered-layered" notation as $xLi_2MnO_3\cdot(1-x)LiMO_2$, have become attractive cathode materials because of their high capacity (>220 mA h g^{-1}) and predominant composition of inexpensive manganese with relatively minor amounts of more costly cobalt and nickel [6–11]. Many studies have been carried out on the synthesis of precursors by using a hydroxide co-precipitation reaction [12,13]. This method, however, is problematic for producing precursors with high manganese content because Mn^{2+} can easily be oxidized to Mn^{3+} (MnOOH) or Mn^{4+} (MnO_2), leading to a formation of heterogeneous sediment [14], which can decrease the homogeneity of the final product. Therefore, it is critical to control the valence state of Mn stable in aqueous solution. Compared with hydroxide co-precipitation method, the carbonate co-precipitation method could keep valence state of Mn^{2+} stable in aqueous solution during precipitation process [14–18], and then it can be used for the synthesis of a more homogeneous and pure lithium- and manganese-rich material with high electrochemical performance.

Unfortunately, due to the complicated composition, the cathode properties of lithium- and manganese-rich material should be sensitively dependent on microscopic features like the distribution of transition metal and the particle morphology. Spherical particles usually have better fluidity and better dispersivity than irregular particles. Therefore, the fabrication of lithium- and manganese-rich cathode materials with spherical morphology is sought to be improve battery performance. The control of the morphology of the precursor is the critical process because the morphology of the cathode material depends on the precursor [19]. It is possible to control the crystallization process using a poor solvent. Ethanol was employed in this work to obtain crystals with the desired size and distribution. Theoretically, ethanol affect the dielectric constant of the medium, the interionic attraction, and the solute–solvent interaction, the understanding of these effects is essential in chemistry of precipitation [20]. Some experts has prepared mono-dispersed $MnCO_3$ [20], calcium phosphates [21,22], calcium carbonate [23] using the ethanol as the additive. The addition of

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ethanol is to obtain spherical and uniform carbonate precursor particles.

In this paper, we investigated the effects of ethanol concentration, reaction temperature (T), and molar ratio of precipitant/total-cations (R) on the physical properties of the precursor ($Ni_{0.15}Co_{0.15}Mn_{0.7}CO_3$) and the electrochemical performance of the final material ($Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$). Among the synthesized materials, the sample prepared with 10 vol% ethanol and a fixed concentration ratio ($[CO_3^{2-}]/[M^{2+}]$=10) at 65 °C exhibited not only a relatively high discharge capacity, but also excellent rate performance and good cycling performance.

2. Experimental

All the reagents used in the present work were of guaranteed grade and used without further purification. Reagents used in this investigation included nickel sulfate hexahydrate ($NiSO_4{\cdot}6H_2O$), manganese sulfate monohydrate ($MnSO_4{\cdot}H_2O$), cobalt sulfate heptahydrate ($CoSO_4{\cdot}7H_2O$), and ammonium bicarbonate (NH_4HCO_3). Equal volume of NH_4HCO_3 solution was added into a mixture of 0.15 mol L^{-1} (0.32 mol L^{-1} for the different concentration ($[CO_3^{2-}]/[M^{2+}]$) ratio experiments) MSO_4 (Ni/Co/Mn:0.15:0.15:0.70) and appropriate volume of ethanol under vigorous agitation in the temperature range from 25 to 75 °C. The precipitated powders were filtered and washed, and then dried at 105 °C overnight. The cathode materials were synthesized by calcination crystallization process using Mn-rich transition metal (Mn, Ni, Co) carbonate precursor and lithium carbonate as raw materials. The obtained carbonate precursors were thoroughly mixed with a stoichiometric amount of Li_2CO_3, then calcined at 950 °C for 10 h in air. The cathode materials were named as LS1–LS12, and the precursors were named as S1–S12, detailed sample preparation conditions were summarized in Table 1.

X-ray diffraction measurements of materials were carried out on a Rigaku 2500 X-ray diffractometer using Cu Kα radiation. The diffraction data were collected over the range $10° < 2\theta < 80°$. The morphological characteristics of the samples were observed by a

Table 1
preparation conditions of $Ni_{0.15}Co_{0.15}Mn_{0.7}CO_3$ precursors.

Sample name	Precursor name	[M]/mol L^{-1}	Concentration of ethanol/vol%	$[CO_3^{2-}]/[M^{2+}]$	Temperature/C
LS1	S1	0.15	0	10:1	55
LS2	S2	0.15	5	10:1	55
LS3	S3	0.15	10	10:1	55
LS4	S4	0.15	15	10:1	55
LS5	S5	0.32	10	10:1	55
LS6	S6	0.32	10	8:1	55
LS7	S7	0.32	10	5:1	55
LS8	S8	0.32	10	2:1	55
LS9	S9	0.15	10	10:1	25
LS10	S10	0.15	10	10:1	40
LS11	S11	0.15	10	10:1	65
LS12	S12	0.15	10	10:1	75

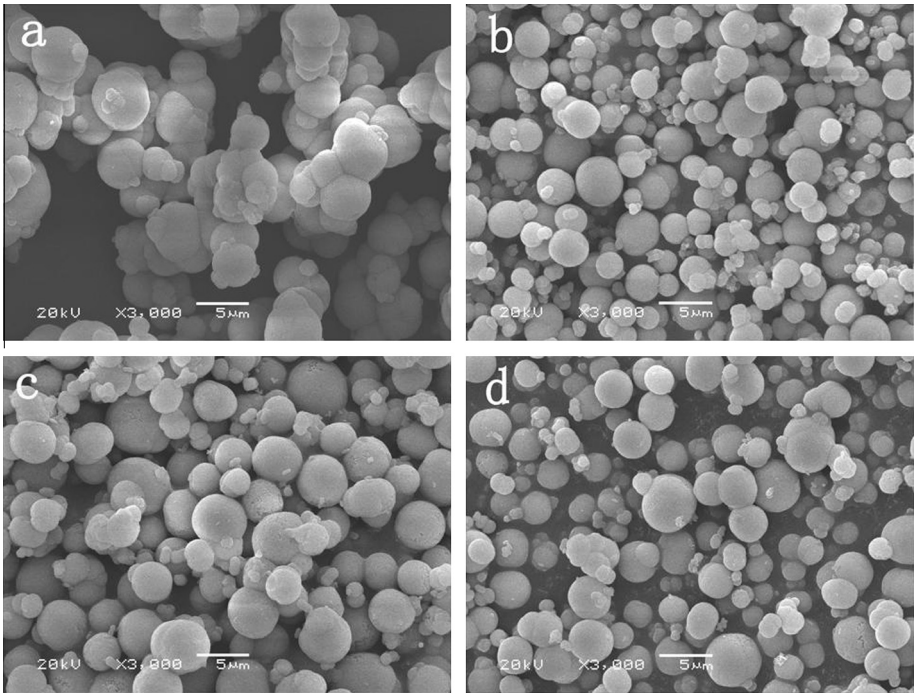

Fig. 1. Scanning electron micrographs (SEM) of the precursors synthesized with various concentration of ethanol: (a) 0 vol% (S1), (b) 5 vol% (S2), (c) 10 vol% (S3), (d) 15 vol% (S4).