Journal of Power Sources 195 (2010) 1486–1494

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Preparation of spherical $LiNi_{0.80}Co_{0.15}Mn_{0.05}O_2$ lithium-ion cathode material by continuous co-precipitation

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ARTICLE INFO

Article history:
Received 8 June 2009
Received in revised form 11 August 2009
Accepted 25 August 2009
Available online 16 September 2009

Keywords:
Lithium battery
Cathode
Continuous co-precipitation
Capacity retention

ABSTRACT

Micro-spherical $Ni_{0.80}Co_{0.15}Mn_{0.05}(OH)_2$ precursors with a narrow size-distribution and high tap-density are prepared successfully by continuous co-precipitation of the corresponding metal salt solutions using NaOH and NH_4OH as precipitation and complexing agents. $LiNi_{0.80}Co_{0.15}Mn_{0.05}O_2$ is then prepared as a lithium battery cathode from this precursor by the introduction of $LiOH{\cdot}H_2O$. The pH and NH_3:metal molar ratio show significant effects on the morphology, microstructure and tap-density of the prepared $Ni_{0.80}Co_{0.15}Mn_{0.05}(OH)_2$ and the R values and $I(003)/I(104)$ ratio of lithiated $LiNi_{0.80}Co_{0.15}Mn_{0.05}O_2$. Spherical $LiNi_{0.80}Co_{0.15}Mn_{0.05}O_2$ prepared under optimum conditions reveals a hexagonally ordered, layered structure without cation mixing and an initial charging capacity of 176 mAhg^{-1}. More than 91% of the capacity is retained after 40 cycles at the 1 C rate in a cut-off voltage range of 4.3–3.0 V.

1. Introduction

Lithium nickel oxide ($LiNiO_2$) with a layered structure has been studied extensively as an alternative cathode material for rechargeable lithium-ion batteries to replace expensive and toxic lithium cobalt oxide ($LiCoO_2$) that is presently used. Commercial application has not been achieved, however, due to difficulties in preparation and property control. It is difficult to introduce a stoichiometric amount of Ni (Li:Ni atomic ratio of 1) into $LiNiO_2$ particles without any divalent nickel in lithium sites. Also, severe capacity fading is observed on repeated charging and discharging cycles, because the structure stability is lower than that of $LiCoO_2$ [1–5]. To circumvent these problems, several types of structure stabilizers, such as transition metals (Co, Mn, Ti, Fe and Zr) and non-transition metals (Mg and Al), have been suggested [6–15]. Among the various stabilizers, cobalt has been shown to hold promise, because it can be substituted in the Ni sites and forms a solid solution of any percentage without affecting the layered structure of $LiNiO_2$. Cobalt modified stabilizers have been found to exhibit enhanced structure stabilization, extended cycleability, and improved charging capacity [16–19]. Nevertheless, the replacement of Ni with Co is limited by the relatively high price of Co and there have been efforts to replace some parts of Ni with cheaper metals such as Mn and Fe. For instance, Hwang et al. [20,21] reported that the substitution of less than 30 at.% of Ni with Mn ($LiNi_{1-x-y}Co_xMn_yO_2$, $y \leq 0.3$) gave improved electrochemical properties [20,21]. Other research has shown improvement in the electrochemical properties of Ni-based cathode materials by coating metal oxides such as ZrO_2 and Al_2O_3 on the surface of particles [22–26].

The electrochemical properties of lithiated mixed transition metal oxides are also influenced by structural properties such as hexagonal ordering, degree of cation mixing, and crystallinity, as well as by chemical composition.

In order to allow use as a cathode material and to guarantee high electric charging capacity, physical properties such as morphology and tap-density also have to be controlled precisely during the synthesis. In general, high tap-density particles can be obtained by increasing the crystallinity and grain size of crystals, but this leads to loss of specific charging capacity. Therefore, there is a limit to increasing tap-density by crystallinity and grain size. Another way to increase tap-density without loss of charging capacity is to fabricate uniform-sized spherical particles, as they can be packed more closely during the coating process of the cathode electrode due to good fluidity. The spherical nature of the particles provides advantages for producing a uniform, stable and dense coating of metal oxides as compared with particles that have an irregular morphology.

As noted earlier, there have been numerous efforts to prepare uniform spherical and high tap-density cathode materials without increasing the crystallinity or the grain size of crystals for high specific charging capacity. Preparation methods for

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doi:10.1016/j.jpowsour.2009.08.101

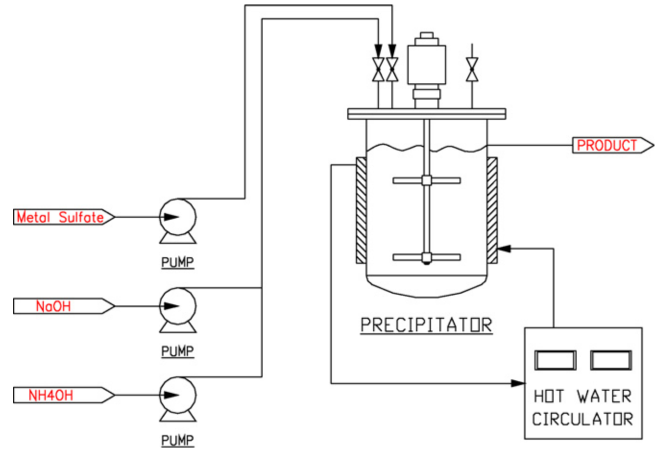

Fig. 1. Experimental apparatus for continuous co-precipitation of $Ni_{0.80}Co_{0.15}Mn_{0.05}(OH)_2$ precursor.

micro-sized spherical powder by controlled crystallization are well described for single and binary oxide systems such as $LiCoO_2$ [27] and $LiNi_{0.80}Co_{0.20}O_2$ [28–34]. Also, many studies have applied co-precipitation methods for the production of a ternary oxide system of Ni, Co, and Mn [35–39]. However, because all of the aforementioned approaches involve preparation in a batch reactor, it is difficult to assess the effect of the synthesis conditions on the morphology and physical and chemical properties. Therefore, in the present work, systematic studies for the preparation of a ternary oxide of Ni, Co, and Mn under continuous precipitation conditions are conducted.

Considering preparation cost, improved tap-density and electrochemical properties brought by Mn to a $LiNiCoO_2$ cathode material, a uniform spherical $LiNi_{0.80}Co_{0.15}Mn_{0.05}O_2$ powder is prepared by a continuous co-precipitation method in aqueous phase using a continuous stirred tank reactor (CSTR). The effect of preparation conditions, such as pH, NH_4OH concentration and co-precipitation time, are investigated and an attempt is made to correlate these conditions with physical and chemical properties. Finally, specific charging capacity tests and a retention analysis are carried out on the prepared $LiNi_{0.80}Co_{0.15}Mn_{0.05}O_2$.

2. Experimental

2.1. *Preparation of $Ni_{0.80}Co_{0.15}Mn_{0.05}(OH)_2$ precursor*

Details of the co-precipitation apparatus are shown in Fig. 1. The continuous co-precipitation of $Ni_{0.80}Co_{0.15}Mn_{0.05}(OH)_2$ was carried out in a specially designed water-jacketed CSTR of 1000 ml capacity. Initially, the reactor was filled to 80 vol.% with distilled water and the pH of the water was then adjusted with 40 ml of 29 wt.% NH_4OH and a few drops of 25 wt.% NaOH solution. The solution was stirred at 500 rpm while maintaining the temperature at 45 °C by circulating hot water through a jacket that enclosed the reactor. 1.5 M aqueous solution of $NiSO_4{\cdot}6H_2O$, $CoSO_4{\cdot}7H_2O$ and $MnSO_4{\cdot}H_2O$ corresponding to a molar composition of 0.80, 0.15 and 0.05, respectively, was introduced continuously into the reactor by a peristaltic pump and the product that overflowed out of the reactor was collected periodically. To induce co-precipitation of metal hydroxides, 25 wt.% NaOH solution was fed into the reactor by another peristaltic pump and the feeding rate was adjusted for desired pH. As a complexing agent, 29 wt.% NH_4OH solution was introduced and the flow rate was regulated by a mass flow controller to maintain the desired NH_3:metal molar ratio. The total feed flow rate was adjusted to maintain an average residence time of 10 h. The product that overflowed out of the reactor was collected periodically for analysis. The precipitation was carried out continuously until both the particle size and morphology reached a steady state. The collected products were neutralized by washing with distilled water and then drying at 110 °C with hot air for 12 h.

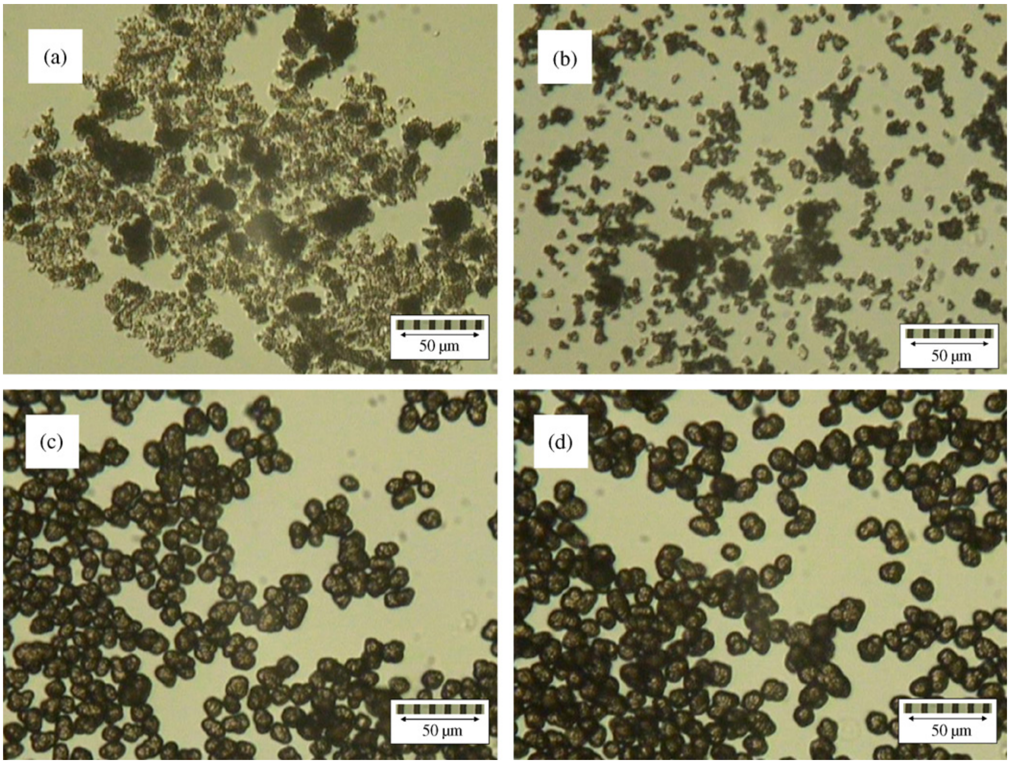

Fig. 2. Optical microscope images of $Ni_{0.80}Co_{0.15}Mn_{0.05}(OH)_2$ depending on precipitation time: (a) 1 h, (b) 8 h, (c) 24 h and (d) 32 h.