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A Co-free layered $LiNi_{0.7}Mn_{0.3}O_2$ cathode material for high-energy and long-life lithium-ion batteries

Seunghyun Ko [a,b], Soon Chang Lee [c], Chul Wee Lee [a,b], Ji Sun Im [a,b,*]

[a] C-Industry Incubation Center, Korea Research Institute of Chemical Technology (KRICT), Gajeong-ro, Daejeon 305-600, Republic of Korea
[b] University of Science and Technology (UST), Gajeong-ro, Yuseong-gu, Daejeon 305-333, Republic of Korea
[c] Department of Fine Chemical Engineering and Applied Chemistry, Chungnam National University, Daejeon 305-764, Republic of Korea

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ABSTRACT

A Co-free layered cathode material, $LiNi_{0.7}Mn_{0.3}O_2$, was synthesized using the co-precipitation method. The optimum conditions for the cathode were determined on the basis of particle size. The relationship between the cathode material's particle size and its lithium-ion battery performance was studied on the basis of the capacity and cyclability. The $LiNi_{0.7}Mn_{0.3}O_2$ material exhibited a high reversible capacity of 176 mA h g^{-1} and a high cyclability, with 98% capacity retention after 40 cycles under the optimum conditions with a specific reaction time. A mechanism based on the structures and morphologies of the synthesized cathode materials is proposed.

1. Introduction

Lithium-ion batteries have been widely used as power sources for portable electronic applications because of their high energy density, good safety and long cycle life. These batteries are also currently used in electric vehicles (EVs) and energy storage systems (ESSs) [1–4]. However, the high cost of the cathode materials for lithium-ion batteries is an issue [5]. Cathode materials account for more than 40% of the cost for a complete battery. The high battery cost is a chief obstacle to the widespread use of lithium-ion batteries.

$LiCoO_2$ is the conventional and most commonly used cathode material [6–9]; however there are high costs associated with cobalt. Considerable efforts have therefore been devoted to developing Co-free cathode materials, such as a layered $LiNi_{0.5}Mn_{0.5}O_2$, to decrease the battery cost.

Ohzuku and Makimura first proposed $LiNi_{0.5}Mn_{0.5}O_2$, which exhibits a reversible capacity of 150 mA h g^{-1} in the voltage range of 2.5–4.3 V [10], as a promising alternative to $LiCoO_2$ [11]. This material has a high degree of a displacement between Li^+ and Ni^{2+}, which degrades its electrochemical characteristics, such as its reversible capacity and rate capability [12]. To overcome this problem, numerous studies have been conducted on aspects such as controlling the molar ratio of transition metals and doping with other elements. Schougaard et al. synthesized $LiNi_{0.56}Mn_{0.44}O_2$, which exhibited an improved capacity, rate capability and cyclability because of the reduced degree of Li^+–Ni^{2+} displacement [13]. A variety of elements have also been doped into this material, including Al, Ti, Mg and Zr, which resulted in improved electrochemical performance [14–16].

However, $LiNi_{0.5}Mn_{0.5}O$ still exhibits low discharge capacity, which must be overcome to satisfy the requirements for large-scale batteries. To obtain higher capacities, the Ni content must be increased [17], because the reversible capacity of $LiNi_{0.5}Mn_{0.5}O_2$ arises from its reversible Ni^{2+}/Ni^{4+} redox reaction with Mn^{4+} in a fixed oxidation state [18,19].

Particle size is one of the most important factors that governs battery performance [20–23]. Depending on the particle size, the surface areas of the electrode materials in contact with the electrolyte [24] and the diffusion length of lithium ions in a particle can vary [25], and these properties are related to the electrochemical kinetics that influence the rate performance. The electrode packing density also depends on the particle size. Particles that are too small will result in a low packing density, thereby increasing the cell resistance [26].

In this paper, we report a Co-free layered cathode material with a Ni-rich composition of $LiNi_{0.7}Mn_{0.3}O_2$ and its battery performance as a function of the secondary particle size. The relationship

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* Corresponding author at: C-Industry Incubation Center, Korea Research Institute of Chemical Technology (KRICT), Gajeong-ro, Daejeon 305-600, Republic of Korea. Tel.: +82 42 860 7366; fax: +82 42 860 7389.

E-mail address: jsim@krict.re.kr (J.S. Im).

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between particle size and battery performance was studied on the basis of structures and morphologies of the prepared cathode materials to elucidate the optimum conditions.

2. Experimental

The cathode material was obtained using a continuously stirred tank reactor (CSTR). As illustrated in Fig. 1, the coprecipitation method was employed to synthesize $Ni_{0.7}Mn_{0.3}(OH)_2$ precursors to the $LiNi_{0.7}Mn_{0.3}O_2$ materials. $NiSO_4{\cdot}6H_2O$ and $MnSO_4{\cdot}H_2O$ were dissolved in distilled water at a molar ratio of Ni:Mn = 7:3. The Ni/Mn molar ratio was derived on the basis of our previous work [27]. The mixed solution was pumped into a 4 L CSTR maintained at 50 °C under a N_2 atmosphere. Simultaneously, a 2 M NaOH aqueous solution as a pH control agent was automatically fed into the CSTR according to the desired internal pH. A 7.5 M NH_4OH aqueous solution was also pumped into the CSTR as a chelating agent. The solutions were then mixed thoroughly in the reactor at a stirring speed of a 900 rpm. Various particle sizes were obtained by controlling the reaction time. The samples were then washed, filtered and dried overnight at 100 °C. The resulting $Ni_{0.7}Mn_{0.3}(OH)_2$ precursors were calcined with $LiOH{\cdot}H_2O$ at 860 °C under an O_2 atmosphere. Finally, the $LiNi_{0.7}Mn_{0.3}O_2$ active cathode materials were obtained. The sample names are listed in Table 1, along with the reaction times for the coprecipitation process. The optimum conditions were investigated over certain reaction times (60–220 h), which were selected on the basis of feasible cathode preparation and cell assembly conditions.

The external morphologies and structures of the prepared cathode materials were examined using scanning electron microscopy (SEM) (VEGA II, Tescan). The particle sizes of the samples were evaluated using a particle size analyzer (Microtrac S3000, Bluewave). X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max-3C diffractometer equipped with a rotating anode and a Cu Kα-radiation source (λ = 0.15418 nm); and the samples were scanned in the 2θ range of 10–80° with a step size of 0.02°. For charge–discharge tests, a WBCS-3000 battery cycler (Xeno Co.) was used. To prepare composite cathodes, we mixed the prepared materials with a conducting agent (Super P) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 90:5:5 in NMP (*N*-methyl-2-pyrrolidone) using a planetary centrifugal mixer (Thinky Mixer, ARE-310). The mixture was then coated onto Al foil and dried in a conduction oven. The as-prepared electrodes were pressed and dried again at 120 °C in a vacuum oven. To investigate the electrochemical performance of the cathode, coin-type cells (CR2032) were assembled in an argon-filled glove box (maintained under 0.1 ppm of O_2 and 1.2 ppm of H_2O) with an electrolyte consisting of 1.0 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 volume ratio) and Li metal as the anode. The loading level of the electrodes was 9.0(±1) mg/cm^2. All of the battery tests were performed at 25 °C over the voltage range of 3.0–4.3 V.

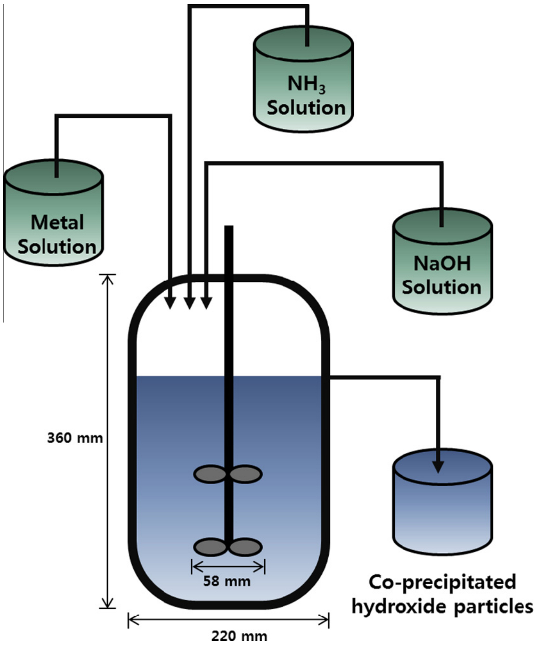

Fig. 1. Illustration of the co-precipitation process employing a CSTR.

Table 1
Reaction time during the coprecipitation process for the prepared samples (H1–H6) and corresponding particle sizes.

Sample name	Reaction time (h)	Particle size (μm)	FWHM in PSA peaks (μm)
H1	60	7.3	4.7
H2	78	9.5	4.9
H3	102	11.7	5.9
H4	112	13.4	6.4
H5	136	17.3	8.6
H6	216	20.4	11.0

3. Results and discussion

3.1. Characteristics of the prepared samples

The relationship between the particle size and reaction time is presented in Fig. 2. We observed that the particle size increased from 7.3 to 20.4 μm in proportion to the reaction time. The particles prepared using this coprecipitation reaction exhibited morphologies similar to that of an agglomerated particle that consists of submicron-sized particles. The agglomerated particles (secondary particles) grew continuously, along with the agglomeration of submicron-sized particles (primary particles) until the reaction ended. This behavior was clearly observed in the SEM images (Fig. 3). All of the samples exhibited the agglomerated morphology, and the particle growth was observed to be dependent on the reaction time. The particles increased in size from 7.3 μm (H1) to 20.4 μm (H6), and the particle morphology changed from an irregular shape to a spherical shape. Overall, from H1 to H6, the particle size increased as the particle shape changed from irregular to spherical.

As shown in Fig. 4, the prepared $LiNi_{0.7}Mn_{0.3}O_2$ materials were confirmed to possess well-defined layer structures according to their powder XRD patterns, which revealed an α-$NaFeO_2$ hexagonal structure with space group $R\bar{3}m$ and no impurity phases. Clearly split doublets of the (108)/(110) and (006)/(102) were also observed, indicating that this material has a highly crystalline layered structure [28,29]. Notably, some nickel ions exist in lithium layers through substitution, which hinders the diffusion of lithium ions; this phenomenon is well known as cation mixing. A schematic is presented in Fig. 5. Cation mixing causes the electrochemical degradation of electrodes, such as changes in their reversible capacity and rate capability [30–32]. The ratio between the integrated intensities of the (003) and (104), $I_{(003)}/I_{(104)}$, indicates the level of cation mixing in a material [33,34]. As the severity of cation mixing increases, the intensity ratio decreases.

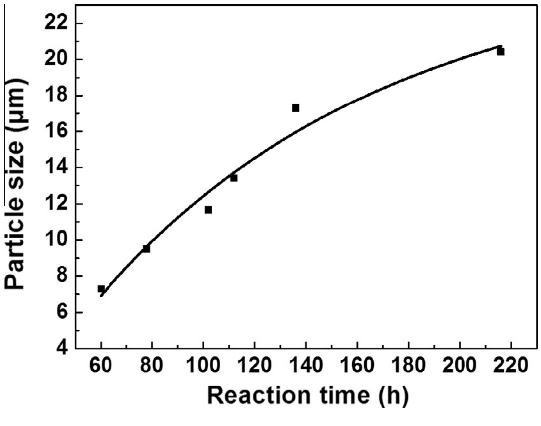

Fig. 2. Particle size distribution as a function of reaction time.