Materials Letters 62 (2008) 4075–4077

Contents lists available at ScienceDirect

Materials Letters

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

Microwave-mediated hydrothermal synthesis and electrochemical properties of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders

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ARTICLE INFO

Article history:
Received 21 February 2008
Accepted 16 May 2008
Available online 22 May 2008

Keywords:
Electroceramics
Composite materials
Microwave-hydrothermal
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

ABSTRACT

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders have been successfully prepared via a newly developed microwave-hydrothermal method. Monophasic powders with an α-$NaFeO_2$ structure were obtained. The particle sizes of the microwave-derived powders were in submicron order (0.2–0.3 μm) and were much smaller than those of the powders synthesized via coprecipitation reaction (1–3 μm). The microwave-hydrothermal route not only shortened the required reaction time but also improved the electrochemical performance of the product. Electrochemical analysis indicated that the microwave-derived $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders exhibited a higher capacity than those derived from coprecipitation method. The capacity fading ratio of the microwave-derived powders was lower than that of the powders obtained via coprecipitation route, according to the results of high C-rate tests.

1. Introduction

Layer-structured $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ has been intensively investigated and viewed as a promising cathode material to be utilized in rechargeable lithium-ion batteries because of its large capacity and good thermal stability [1–3]. The crystal structure of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ oxide is categorized as an α-$NaFeO_2$ type structure with a rhombohedral $R3m$ symmetry. The valence states of nickel, cobalt, and manganese ions in $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders are 2+, 3+, and 4+, respectively [3]. Only divalent nickel ions and trivalent cobalt ions are electro-active, involving $Ni^{2+/4+}$ and $Co^{3+/4+}$ redox couples [3]. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ reportedly had a high rechargeable capacity ranging from 2.5 to 4.6 V [4].

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders are generally synthesized via solid-state reaction and coprecipitation method [5,6]. High temperature heating in the solid-state process usually results in unfavorable grain growth and non-uniform morphology. On the other hand, the coprecipitation method requires a series of sophisticated operations during the preparation processes. Developing a new synthesis route for preparing $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders with improved electrochemical performance is therefore crucial.

Recently a microwave-mediated radiation process has been employed to synthesize ceramic powders [7,8] due to its advantages of rapid volumetric heating, increased reaction rates, good homogeneity, and high reproducibility. Incorporating rapid microwave heating into hydrothermal processing possesses a good potential for synthesizing new inorganic materials. A new microwave-hydrothermal method was developed in this study to produce $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders. The structural development, morphological evolution, and electrochemical characteristics of the microwave-derived $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were investigated. The microwave-derived $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were also compared with those obtained via the coprecipitation route in respect of their electrochemical properties.

2. Experimental

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were prepared via two different methods: the coprecipitation and microwave-hydrothermal processes. The coprecipitation method (abbreviated as C-P method) prepared $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$ precursors from a mixed aqueous solution of $Ni(NO_3)_2$, $Co(NO_3)_2$, and $Mn(NO_3)_2$ with a cationic ratio of Ni^{2+}:Co^{2+}:Mn^{2+} = 1:1:1. The concentration of transition metal-ion solution was set at 1 M. Precipitation was achieved by slowly dripping LiOH (1 M) into the above solution with continuous stirring. The pH value of the solution was around 12, and stirring procedure was continued for 24 h. The filtrated precipitates were washed with deionized water repeatedly to remove residual ions, followed by drying the obtained powders at 70 °C in air for 12 h.

On the other hand, $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$ precursors were also prepared via the microwave-hydrothermal method (abbreviated as M-H method). The mixed transition metal nitrate (Ni^{2+}:Co^{2+}:Mn^{2+} = 1:1:1) solution (1.0 M) and LiOH (1.0 M) aqueous solution were simultaneously added into a double-walled vessel. The microwave reaction was carried out in a microwave digestion system (MLS 1200 Mega) operating at 2450 MHz with the radiation temperature fixed at 180 °C. The pressure attained during the microwave processing was around 10 bar and the reaction time was 20 min. $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$

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doi:10.1016/j.matlet.2008.05.034

precursors were obtained after the microwave reaction. The formed powders were then filtrated, washed, and dried in air.

$(Ni_{1/3}Mn_{1/3}Co_{1/3})(OH)_2$ powders synthesized via either the coprecipitation route or microwave-hydrothermal method were mixed thoroughly with a stoichiometric amount of LiOH powders. The mixtures were calcined at 800 °C in air for 3 h, and the resultant products were ground for further characterization. The crystal structure of the obtained powders was analyzed via X-ray diffraction (XRD). Scanning electron microscopy (SEM) was performed to examine the microstructures of the powders. The cathodes were prepared by mixing $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders, KS6 graphite, super-P carbon black, and PVDF in a weight ratio of 85:5:2:8, using NMP as the solvent. Lithium foil was utilized as the anode, and the electrolyte solution was composed of 1 M of $LiPF_6$ dissolved in EC/DEC (1:1 in volume ratio).

3. Results and discussion

Fig. 1 illustrates the XRD patterns of $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$ prepared via (a) M-H and (b) C-P methods. The obtained precursors were composed of $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$. The precursors derived from M-H method had greater crystallinity than those derived from C-P method. Upon calcination at 800 °C, the precursors prepared via both methods were transformed into $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ as shown in Fig. 1(c) and (d). The peaks in both patterns indexed to a hexagonal α-$NaFeO_2$-type layered structure belonging to the $R3m$ space group (No. 166). The comparison between Fig. 1(c) and (d) shows that the diffraction peaks of powders derived via M-H method were sharper than those of powders synthesized via C-P method, indicating superior crystallinity of microwave-derived $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders. The lattice parameters of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders obtained via M-H process were calculated to be a=2.860(2) Å and c=14.227(8) Å using a least-square method (c/a=4.97), and these values matched well with those reported by Ohzuku and Makimura [1]. The ratios of the integrated intensity of (003) peak to that of (104) peak in Fig. 1(c) and (d) were calculated to be 1.56 and 1.42, respectively. The intensity ratio of $I_{(003)}/I_{(104)}$ peaks was reportedly regarded as a cationic mixing index, in which smaller $I_{(003)}/I_{(104)}$ values suggesting lesser cationic mixing [9]. The above results confirm that $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders prepared via M-H route had minimal cationic mixing and a well-ordered layered structure.

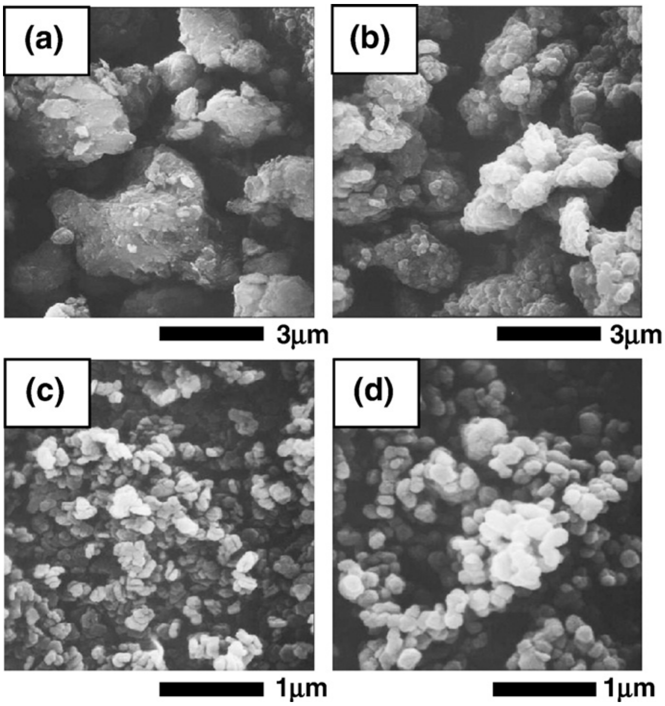

Fig. 2. Scanning electron micrographs of coprecipitation-derived (a) $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$ and (b) $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders and microwave-derived (c) $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$ and (d) $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders.

Fig. 2 shows the SEM photographs of (a) $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$ and (b) $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders prepared via C-P process. Both samples exhibited non-uniform and agglomerated morphology. The particle sizes of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders synthesized via C-P method ranged from 1 to 3 µm according to the corresponding micrograph. The microstructures of $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders obtained via M-H process are shown in Fig. 2(c) and (d). The microwave-derived $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$ powders exhibited homogeneous morphology with small particle sizes ranging from 50 to 100 nm. It is observed from Fig. 2(d) that microwave-derived $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders exhibited spherical morphology with narrow particle size distribution in the range of 0.2 to 0.3 µm. By comparing Fig. 2(b) with (d), it is clearly demonstrated that M-H process significantly reduced the particle sizes of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders. The motion of constituent ions in M-H reaction is accelerated under the influence of electric field [10]. The fast moving ions are considered to collide with particles, and the particle size of the prepared powders is consequently reduced. For the microwave-derived precursors, the improved crystallinity accelerated the reaction of the starting materials and the reduced particle size shortened the diffusion length between the constituent components. Therefore, M-H method significantly shortened the required calcination time for obtaining pure $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$.

Fig. 3 illustrates the charge–discharge curves (C/5 rate) of 800 °C-calcined $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders prepared via (a) M-H and (b) C-P methods. Based on Fig. 3(a), the first charge and discharge capacities of the powders obtained via M-H method were

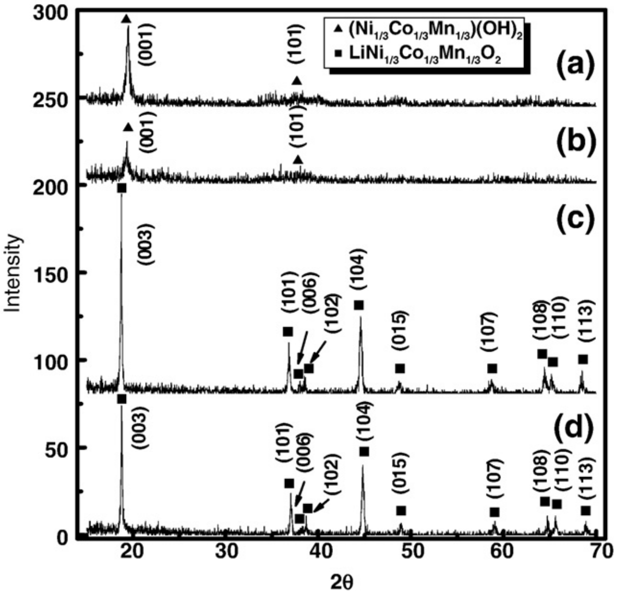

Fig. 1. XRD patterns of microwave-derived (a) $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$ and (c) $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, and coprecipitation-derived (b) $(Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)_2$ and (d) $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$.

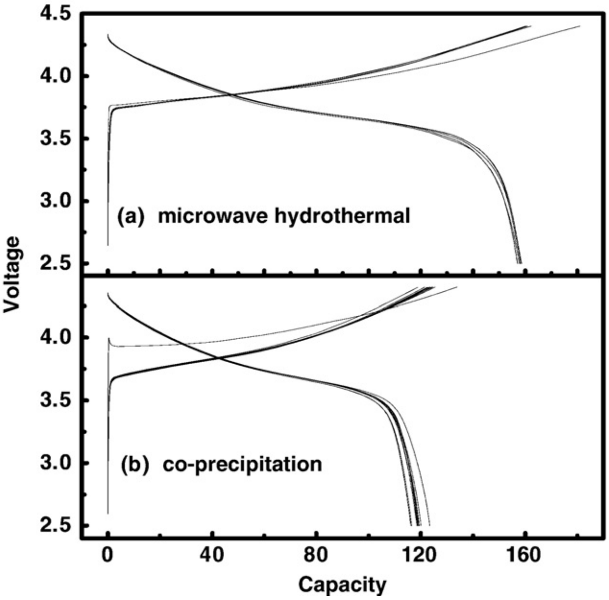

Fig. 3. Charge and discharge characteristics of (a) microwave-derived and (b) coprecipitation-derived $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders calcined at 800 °C for 3 h.

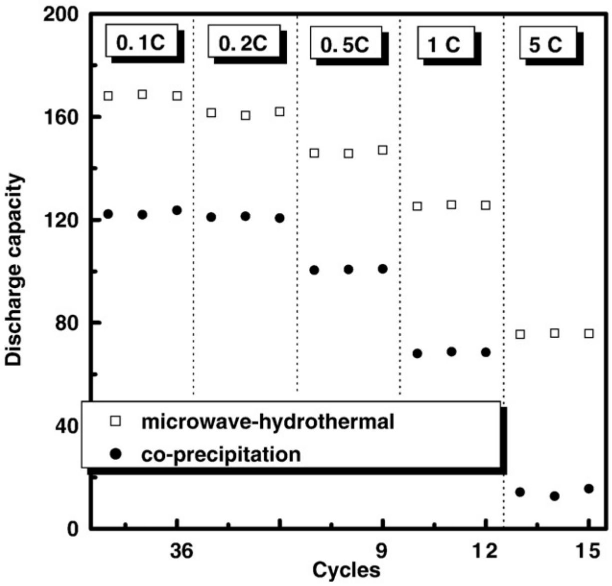

Fig. 4. Relations between discharge capacities of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders and cycle number at different C-rates.

181.1 and 157.8 mAh/g, respectively. The curve shows that the discharge capacities increased slightly in the initial cycle and reached a plateau after four cycles. The discharge capacity was 156.0 mAh/g after ten cycles, approximating 98.8% of the value in the initial cycle. On the other hand, the discharge capacity of coprecipitation-derived $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders in the first cycle was merely 123.4 mAh/g. After ten cycles, the discharge capacity decreased to 116.2 mAh/g and the discharge capacity retention was 94.1%. The microwave-derived powders exhibited larger capacities and higher retention as compared with those prepared via the coprecipitation route. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders synthesized via the microwave-hydrothermal process had enhanced crystallinity with reduced particle size, leading to improved electrochemical performance.

Rate capabilities of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders prepared via M-H and C-P methods at different C-rates are illustrated in Fig. 4. At 0.1 C, the discharge capacities of the powders obtained via M-H and C-P methods were 168 and 123 mAh/g, respectively. Moreover, the discharge capacities of the microwave-derived and coprecipitation-derived powders reduced respectively to 75 and 15 mAh/g when C-rate was raised to 5 C. Accordingly, the powders prepared via M-H method had a much lower fading ratio (55.3%) than those obtained via C-P methods (87.7%). These results indicate that microwave-derived $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders exhibited higher discharge capacities at different C-rates and better rate capability than the coprecipitation-derived powders. It is suggested in this study that $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders with reduced particle sizes provide more surface area for contacting with liquid electrolyte, thereby facilitating the intercalation and de-intercalation of lithium ions in the host structure [11,12]. As a result, the powders derived via the microwave-hydrothermal process exhibit better rate capability than the coprecipitation-derived powders. Successful synthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders having high specific discharge capacities and good rate capability proved the feasibility of this microwave-hydrothermal process. The developed microwave-hydrothermal process is also considered applicable to synthesize other types of cathode materials to be utilized in lithium-ion secondary batteries.

4. Conclusions

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were successfully prepared via a newly developed microwave-hydrothermal process. This process not only significantly shortened the required reaction time for preparing the precursors, but also effectively decreased the particle size of the obtained powders from 1–3 μm to 0.2–0.3 μm as compared with the coprecipitation method. The powders prepared via the microwave-mediated hydrothermal process exhibited high discharge capacities and good cycleability. Microwave-derived powders in the high C-rate tests showed excellent rate capabilities. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders with improved electrochemical performance and reduced particle size were successfully synthesized via the microwave-hydrothermal method. It is demonstrated in this study that the microwave-hydrothermal method ought to be a promising technique for preparing $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ materials with enhanced electrochemical performance.

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