

Short communication

Synthesis of $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material using spray-microwave method

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Abstract

Spherical particle morphology of $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material was carefully controlled by spray drying the slurry containing mixed oxides pre-calcined at 900 °C. The as-dried powders were then treated in a microwave-processing cavity with different power and time. The microwave-processing cavity is a designed elliptically resonant cavity with double foci. One focusing zone concentrated microwave energy to treat the as-dried cathode material. After microwave-treated power of 200 W for 15 min at least, high purity of Rocksalt structure showed high ratio of integrated intensities of (003)/(104), larger than 1.1, and double peaks (006)/(102) and (108)/(110) split up clearly based on X-ray diffraction patterns. After 200 W microwave treating for 15 min, the discharge capacity of the obtained $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders was 120 mAh g⁻¹ by charging from 4.3 to 2.5 V at room temperature. Furthermore, discharge capacity larger than 140 mAh g⁻¹ can be obtained for treating with 200 W microwave energy for 30 min. Nevertheless, the discharge capacity was less than 100 mAh g⁻¹ treated with 1100 °C/24 h by conventional furnace. The microwave-treated $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material sustains capacity less than 5% degradation after 50 cycles test. The results of microwave process show promise properties requirement for commercial applications.

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1. Introduction

Multi-components lithium ion secondary battery materials of $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$, although the difficult stoichiometric control, are intensively developed due to their potentially high discharge capacity, excellent cycling stability, safe and cost-effective to replace LiCoO_2 as cathode materials [1–3]. There are many problems to be concerned in commercially available cathode materials. The LiCoO_2 cathode material shows high capacity and excellent cycling stability [4], but the cost and environmental pollution problems limited in large scale for Li-ion battery application. Cobalt is the most expensive component as compared with nickel, manganese, etc. The LiNiO_2 easily

decomposes into Li-deficient compounds due to reduction of Ni^{3+} and lithium evaporation at high synthesizing temperature [5]. LiMn_2O_4 has a spinel structure, cost effective and small environmental impact. The most disadvantage is slow fading capacity [6].

Although, the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is appreciated to be a cathode material to replace Li–Ni, Li–Co or Li–Mn oxides for commercial applications, difficult stoichiometric preparation such as Ni^{2+} occupied at 3a site of Li^+ and poor cycling stability are still necessary to overcome [2,3,7–9]. In a Li-ion battery, a large surface area is necessary to increase the contact area between active material, conductive additive, and electrolyte. Therefore, it is an important role of cathode material's surface morphology on the rate performance. On the other hand, lower processing temperature suits the existence of a higher valence of nickel. Therefore, pre-controlling compositions, particles morphology and low

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temperature synthesizing process are undergoing to develop [1,2,4,9,10].

However, the commercialized cathode materials powders are usually prepared via conventional solid-state reaction of mechanically mixed lithium compounds and transition metals oxides. The obtained powders always show irregular particle morphology with broad particle size distribution. The synthesizing temperatures are relatively high, at least 1100 °C, and long soaking time, generally 24 h [10]. In general, chemical processes are utilized to improve the drawbacks of conventional solid-state reaction, but multi-steps, time-consuming and processing conditions controlled precisely are commonly required.

The microwave processing is a viable route for the synthesis of many inorganic materials and the sintering of advanced materials [11–13]. A great deal of interest has been shown in the microwave-assisted synthesis of cathode materials such as LiMn_2O_4 [14–17], LiCoO_2 [18,19], LiNiO_2 [20] and LiFePO_4 [21]. Those reports indicate microwave process beneficially in grain size control, promise electrochemical charge–discharge cycle performance for cathode materials. However, most of microwave process researches pay attention on single transition metal cathode materials.

In this work, the lithium ion battery cathode material consisted of multiple transition metals was synthesized and studied by spray drying combined microwave process. The intensified electromagnetic energy was focused on a focus region of an elliptical microwave cavity. The pre-calcined mixed oxides cathode materials were spray-dried through a furnace to control the particles morphology then synthesized in the designed microwave cavity. The efficient microwave-cathode material interaction to synthesize single phase of $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was investigated with various microwave power and time. Thus, obtained morphology and phase control $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material was further compared to those prepared by the conventional process.

2. Experimental

Reagent grade starting materials of NiO (99%, SHOWA), MnO_2 (99%, STREM), Co_3O_4 (99%, STREM) and Li_2CO_3 (99%, MERCK) were utilized to prepare formula of $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, termed as LNCM. The excess 10 mol% of Li was used to promote the appearance of Ni^{3+} and to compensate the possible volatilization in processing [3]. Such starting materials mixed with de-ionized water were milled for 20 h. After the ball-milled slurry was dried in an oven, the dried cake was pulverized by pestle and mortar, subsequently calcined at 900 °C/2 h in an electrical furnace. The calcined powders were further ball-milled for 4 h to prepare slurry for spray drying by an atomizer.

A part of slurry was dried and ground, then that was further heat-treated in conventional furnace at a temperature of 1100 °C for 24 h to synthesize $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material. Another part of slurry of calcined powders was spray-dried through a tube furnace set at 400 °C to granulate the spherical particles and the dried powders were collected at the outlet

of tube furnace. Those as-dried powders were then treated by microwave energy.

An elliptical microwave cavity was designed such that one of the foci of the ellipse couples an electromagnetic (EM) energy into the cavity and the other focus concentrates the coupled energy to enable microwaves processing utilities. The EM field pattern indicates that the intensified energy is in the single mode and is homogeneously distributed throughout the 1 in. region of the elliptical foci. The microwave generator is a commercial 2.45 GHz magnetron head adapted by adding a WR340 waveguide to output the wave. The spray-dried powders were in a quartz tube, 20 mm diameter by 50 mm height, adhered to a quartz rod clamped by a rotating motor. The quartz tube was inserted into focus region of microwave cavity and was rotatable in microwave process. A refractory material was used to surround the quartz tube to prevent the heat loss from the heating powders. Microwave processed powers were 100–400 W, processed time was 5–30 min. All the synthesized cathode materials, which from both of conventional and microwave process, were screened by 100-mesh screener.

The processed powders were analyzed using a field emission-scanning electron microscope (FE-SEM, LEO 1530) to characterize the microstructure, and morphology. The crystal structure was characterized by X-ray diffraction (XRD, Rigaku D/MAX-IIB, Cu $K\alpha$ radiation wavelength $\lambda = 1.5405 \text{ \AA}$, scan speed of 4°/min). The induced coupling plasma-optical emission spectrum (ICP-OES, spectro-FLAME) analyzer was used to analyze the elements in LNCM composition. The synthesized cathode material via paste preparation, coating and cutting was assembled by 2032 type coin cell for electrochemical performance test. Such cathode materials were prepared by mixing $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, carbon black and PVDF in a weight ratio of 84:8:8 in NMP. Li metal foils, PP, LiPF_6 (1M) with ethylene carbonate/ethyl methyl carbonate, 1:2 by volume ratio (EC/EMC) were used as anodes, separators, and electrolytes, respectively. The oxidation–reduction potential was carried out by cyclic voltammogram (CV). The cycling was galvanostatically performed at constant charge–discharge current of 0.1 C between 2.5 and 4.3 V and the cycle time with 1 C–1 C rate at room temperature.

3. Results and discussion

The phase transformation of mixed oxides by conventional process was shown in Fig. 1. The X-ray diffraction (XRD) pattern showed incomplete phase change in mixed oxides calcined at 900 °C/2 h. Clearly hexagonal layered structure of $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (LNCM) was achieved after 1100 °C/24 h heat-treated the calcined powders. It indicated that the synthesis of LNCM from mixed oxides by conventional electrical furnace treating needed precalcination and enough long soaking time at high heat-treatment temperature to transform the hexagonal layered crystal structure completely.

The spray-dried pre-calcined mixed oxides, morphology as shown in Fig. 3(b), were microwave-treated with various powers for 5 min, the crystal structures as shown in Fig. 2(a). The Rocksalt crystal structure of the LNCM was obtained by the

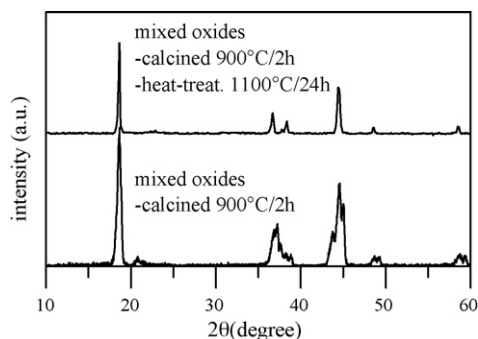


Fig. 1. X-ray diffraction patterns of mixed oxides that were heat-treated by conventional process 900 °C/2 h and further 1100 °C/24 h.

microwave power larger than 100 W. It is clear that the integrated ratio of peaks (003)/(104) increases and peaks (006)/(102) split up more clearly when the microwave energy increases. But the secondary phase was observed by X-ray diffraction when the microwave power larger than 400 W (not shown). It may be the microwave–material interaction too drastically to decompose the cathode materials, e.g., lithium volatilization. This consideration was referenced to Fig. 3(c). The slight melting and grain growth in Fig. 3(c) were the result of microwave-treated 300 W/5 min. It indicated the violent interaction occurrence in such microwave process condition.

The hexagonal layered crystal structure was developed more completely with the increase of microwave-treated time at power level of 200 W, as shown in Fig. 2(b). It presents that the integrated intensity ratio of peaks (003)/(104) increases and peaks (006)/(102) split up more clearly when the treated time increases. It meant extension of microwave-treated time at 200 W facilitated the hexagonal layered crystal structure development. The crystal microstructure of microwave treatment at 200 W for 15 min was shown in Fig. 3(d). It shows clear hexagonal planes and the lattice growth is along with the *c*-axis. From the results of Figs. 2(b) and 3(d), XRD peaks broadened and peaks intensity decreased slightly were supposed grain growth with longer soaking time, beneficially ions diffusion.

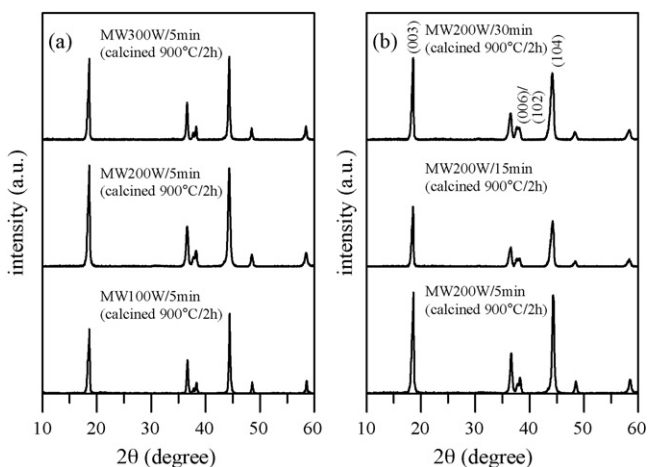


Fig. 2. X-ray diffraction patterns of cathode materials treated with (a) various microwave power for 5 min and (b) various soaking time for 200 W microwave power. The cathode materials were pre-calcined at 900 °C/2 h.

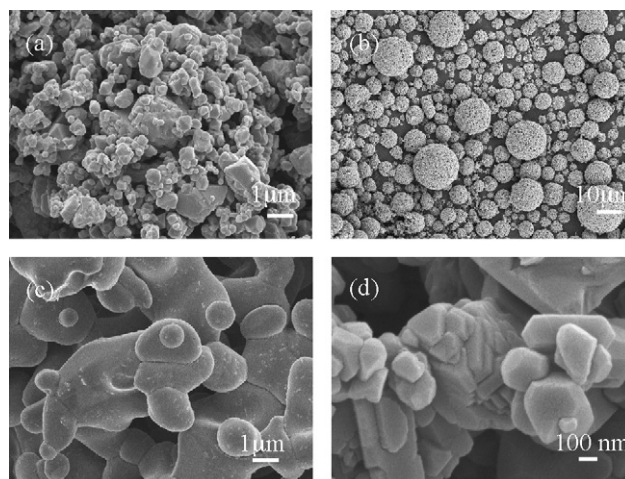


Fig. 3. Microstructures of powders in various treated steps, (a) 900 °C/2 h calcination by conventional electrical furnace, (b) spray-dried spherically granules of 900 °C/2 h calcined particles, (c) microwave treatment 300 W/5 min and (d) microwave treatment 200 W/15 min.

The 900 °C/2 h calcined powders showed a large range of particle size distribution and extremely irregular morphology, as shown in Fig. 3(a). The spherical aggregates of primary particles were successfully achieved by spray-dried with an atomizer through a tube furnace at 400 °C, as shown in Fig. 3(b). The adequate crystal development of microwave-treated particles is confirmed as the microstructure in Fig. 3(d) and XRD in Fig. 2(b).

In Fig. 4, the electrochemical properties galvanostatically measured at constant charge–discharge current of 0.1 C between 2.5 and 4.3 V at 20 °C exhibit the discharge capacity for different microwave-treated time at 200 W. It shows nearly the same discharge capacity for 5 and 15 min treatment, but significant increase for 30 min. It was believed well-developed hexagonal layered crystal structure and adequate grain growth enhanced the high discharge capacity for 200 W/30 min microwave-treated samples.

In Fig. 5, it shows the comparison of microwave and conventional processed LNCM cathode materials for their charge–discharge characteristics. It is obviously higher discharge capacity of microwave treatment at 200 W for 30 min than that of conventional treatment at 1100 °C/24 h. High discharge property, i.e., low irreversibility, indicated that the crystallinity, microstructure, morphology and composition homogeneity of cathode materials synthesized by spray-microwave pro-

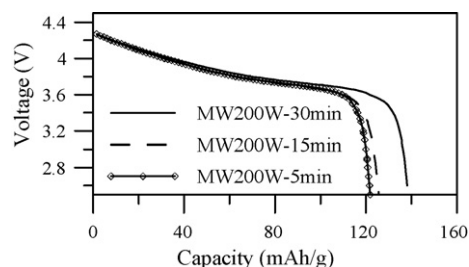


Fig. 4. Discharge capacity of cathode materials microwave-treated with different soaking time by 200 W microwave power.

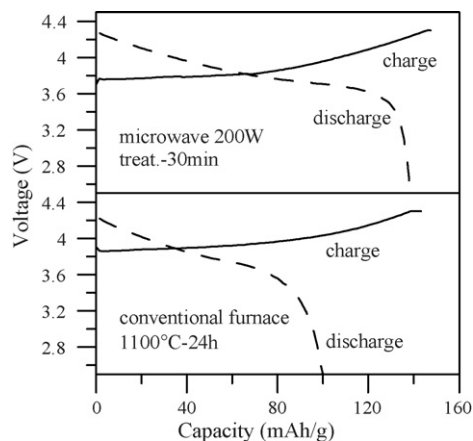


Fig. 5. The charge–discharge comparison of microwave and conventional process.

cess were superior to conventional process. Furthermore, the 200 W/30min microwave-treated cathode material tested the cycle time with 1C–1C rate at room temperature. The result is shown in Fig. 6, indicating the capacity less than 5% degradation after 50 cycles test. Those results of microwave process showed promise properties requirement for commercial applications.

In order to identify the interaction degree of both of microwave and conventional processes, the cathode materials synthesized by microwave treatment 200 W/30min and conventional treatment 1100 °C/24 h were analyzed by ICP-OES chemical analysis method to obtain the mole ratio of elements Li, Ni, Co and Mn. The obtained mole ratios were calculation from the average weight percentage of two analyzed data for each elemental analysis. For both of microwave and conventional processes, the mole ratio of Ni:Co:Mn almost maintains the ratio of 1/3:1/3:1/3 with respect to $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, as referred to Table 1. However, the lithium loss in conventional process of 1100 °C/24 h is obviously larger than that in microwave process of 200 W/30min. It was believed that the high temperature in conventional heat-treatment resulted in the high loss of lithium. It was the reason of low discharge capacity and short cycling time in conventional heat-treatment in comparison with microwave treatment.

Similar to high temperature induced the volatilization of lithium in conventional process 1100 °C/24 h, too high

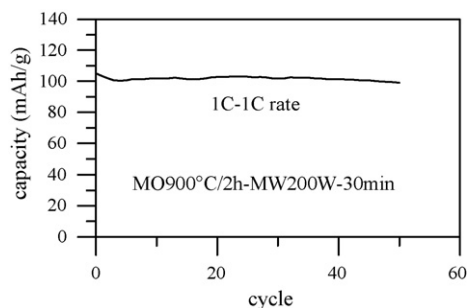


Fig. 6. The discharge capacity with the cycle time with 1C–1C rate at room temperature for 200 W/30min microwave-treated cathode material.

Table 1

The elemental analysis of $\text{Li}_{1.1}(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})\text{O}_2$ for elements Li, Ni, Co and Mn by ICP-OES method^a

Sample	Li	Ni	Co	Mn
Microwave, 200W/30 min	1.034	0.334	0.329	0.339
Conventional furnace, 1100 °C/24 h	0.921	0.339	0.338	0.344

^a The mole ratios were calculated from weight-percent of two repeated ICP-OES data of respective analyzed element.

microwave power, e.g., 400 W, was going to be the same result of lithium loss. Different microwave energy absorbed by cathode materials would evolve different temperature. The equivalent temperature of various input microwave power was calibrated by use of Pt–13%Rh thermocouple shielded with alumina tube in contact with the quartz tube having cathode materials inside. The equivalent temperature is about 750 °C to 200 W, 900 °C to 300 W and 950 °C to 400 W. It was understood that the violent interaction during microwave energy provision, more efficient energy to cathode materials than the conventional electrical energy did. Furthermore, that the effective temperature 750 °C by 200 W microwave energy can synthesize LNCM cathode materials with short processing time of 30 min was thought as the high microwave absorption ability of transition species. After the reaction of optimum microwave energy, i.e., optimum effective temperature 750 °C, the cathode materials may be with high valence of transition elements in them to stabilize the crystal structure and to be beneficial the electrochemical properties.

4. Conclusion

Hexagonal layered structure of $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (LNCM) was achieved clearly after 1100 °C/24 h heat-treatment but not 900 °C/2 h in conventional process. The LNCM crystal structure was already obtained by the microwave power larger than 100 W. It is clear that the integrated intensity ratio of peaks (003)/(104) increases and peaks (006)/(102) split up more clearly when the microwave energy increases. Too large microwave power, larger than 300 W, treated LNCM material would result in possible melting because of near the edge of thermal runaway. Microwave power of 200 W presented the integrated intensity ratio of peaks (003)/(104) increased and peaks (006)/(102) split up more clearly when the soaking time increased. The discharge capacity 140 mAh g^{-1} by 200 W/30min microwave heat-treatment was far higher than 100 mAh g^{-1} by 1100 °C/24 h conventional heat-treatment. The discharge capacity of 200 W/30min microwave-treated cathode material was less than 5% degradation after 50 cycles test with 1C–1C rate at room temperature. The equivalent temperature about 750 °C to 200 W microwave input power was enough to reduce lithium volatilization significantly and to stabilize the high valence of transition elements to achieve stoichiometric composition of $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and then promise electrochemical properties.

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