



Contents lists available at ScienceDirect

Journal of Power Sources

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

Full microwave synthesis of advanced Li-rich manganese based cathode material for lithium ion batteries

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HIGHLIGHTS

- Full microwave synthesis is performed to obtain Li-rich oxides within 60 min.
- Such method exhibits high time-efficiency and power economization.
- Stable surface with desired Mn, Co, Ni states and less impurity is obtained.
- High discharge capacity of 159.3 mAh g⁻¹ is obtained at 2000 mA g⁻¹.
- 88.6% capacity is remained after 300 cycles at such high current density.

ARTICLE INFO

Article history:

Received 3 September 2016

Received in revised form

14 October 2016

Accepted 29 October 2016

Available online xxx

Keywords:

Full microwave synthesis

Time-efficiency

Li-rich layered oxides

Cathode material

Lithium ion battery

ABSTRACT

In technologically important Li-rich layered cathode materials, the synthesis time is a critical determinant to overcome the practical difficulties. Normal technology costs at least one day or even more to obtain final Li-rich cathode material. Full microwave synthesis is performed here to obtain final $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$ within 60 min with high time-efficiency and power economization. The as-prepared Li-rich oxides keep the spherical hierarchical structure of the precursor. Compared to the same material obtained by traditional calcination, it exhibits well-formed layered structure with higher ordered ion arrangement. X-ray photoelectron spectroscopy (XPS) indicates that microwave assisted heating contributes to a more ordered and stable surface with desired Mn, Co, Ni element states and less impurity. Thus, the as-prepared material reveals remarkable electrochemical property with high discharge capacity of 159.3 mAh g⁻¹ at high current density of 2000 mA g⁻¹. And 88.6% specific capacity is remained after 300 cycles at such high current density. Furthermore, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT) are carried out to overall investigate and estimate the material. It is concluded that such full microwave synthesis is really promising as one of the dominant way to obtain Li-rich layered cathode material for applications.

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1. Introduction

The development of lithium ion batteries (LIBs) has fulfilled the major technology breakthroughs in power tools, portable electronics, hybrid electric vehicles (HEV) and electric vehicles (EV) [1]. Among the component of LIBs, cathode material is considered to be the primary determinant breakthrough for enhanced energy and power delivery. Thus, cathode materials have received considerable

attention, especially for Li-rich manganese based layered oxides (also known as $\text{xLi}_2\text{MnO}_3 \cdot (1-x) \text{LiMO}_2$, $\text{M} = \text{Mn, Ni, Co}$) which exhibits high specific capacity, high energy density, environment benignancy and relative low cost [2–4]. Nevertheless, its poor electronic conductivity, unstable surface structure under F contained commercial electrolyte, time-consuming synthesis as well as the disadvantage resulting from the initial activation, significantly restrict its application as high energy cathode material for lithium ion batteries [4–6]. A lot of approaches have been investigated to overcome the above deficiency, such as surface treatment [2,7–12], controllable construction of the material morphology [13–18], and so on. Then, Li-rich layered oxides with high rate capability,

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excellent cycle stability can be obtained. However, few studies are carried out about high efficient synthesis with less time and power.

Nowadays, numerous methods have been applied to obtain Li-rich manganese based oxides with excellent electrochemical properties, such as solid state reactions [19], co-precipitation [20–22], freezing drying method [23], sol-gel method [24–26], combustion method [27,28], molten salt method [29] and so on. All these methods inevitably suffer from a real long synthesis time. And a comparison of different synthesis methods to obtain Li-rich oxides reported has been listed in Table 1. Usually, at least several hours or more are necessary for the formation of Li-rich manganese based layered oxides under high temperature (800–1000 °C) in air. The Li ions must migrate and react with the ternary precursors (usually MCO_3 or $\text{M}(\text{OH})_2$, $\text{M} = \text{Mn, Ni, Co}$) by solid diffusion. Thus, it is not only time-consuming but also power-wasting to offer such a high temperature atmosphere for such a long time. Method with high time-efficiency must be studied to shorten the synthesis time and economize the power. Furthermore, atomic migration under traditional calcination usually will lead to undesirable particle growth and deficiency [30].

Microwave-assisted preparation has recently been used to synthesize cathode material for lithium ion batteries due to its rapid and uniform heating through the vibration of the material molecule itself within several minutes. Cathode materials such as LiV_3O_8 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ have been successfully obtained by microwave assisted solid-state reactions and exhibit excellent electrochemical properties [30–33]. However, few studies about Li-rich manganese based layered oxides with microwave synthesis are reported, especially for full microwave synthesis. Because of the particularity of ternary Li-rich manganese based layered oxides, the whole reaction processes must avoid the re-congregating of Mn, Ni, Co elements themselves to keep a molecular level mixture. Then, ternary Li-rich manganese based layered oxides with great property could be obtained as cathode materials for LIBs. The way of full microwave synthesis can efficiently cause violent vibration of the material molecule to increase the degree of molecular confusion and stop the re-congregating of Mn, Ni, Co.

In our previous work [34], we shorten the synthesis time of the ternary precursor within 30 min by rapid microwave hydrothermal method. However, a long time traditional calcination is not shunned. Here, in the present work, full microwave synthesis is applied to further cut the total synthesis time down to 60 min. Such method not only shortens the synthesis time, economizes the power, but also can obtain well formed $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$ cathode material. Furthermore, full microwave synthesis seems to change the structure and surface element states of $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$, resulting in enhanced electrochemical properties.

2. Experimental

2.1. Materials preparation

The preparation of the precursor of Li-rich layered compound $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ is the same as our previous work [34]. The precursor was then mixed with stoichiometric amounts of $\text{LiOH} \cdot \text{H}_2\text{O}$ using ethanol as the medium to ensure a thorough mixture. After drying, the mixture was divided into three shares. One was calcined in a traditional furnace at 900 °C for 16 h in air to get Li-rich layered compound $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$, which is named as TH960m for short. The other two shares were calcined in a microwave high temperature furnace (SYNO-THERM) at 900 °C for 10 min and 60 min in air, respectively, and named as MW10m and MW60m for short.

2.2. Material characterization

The data of X-ray diffractometry (XRD) was collected at a fixed step width of 0.02° using Cu K α radiation from 10° to 90° on X-ray diffractometer (D/max-2200-PC). Counting time duration of 8.0 s was set for each step. The XRD profiles were then fitted using Rietveld refinement with the Rietveld Program (GSAS). In order to further study the structure of the material, the atomic distribution and cell parameters were calculated according to the results of the refinement. Field emission scanning electron microscopy (SEM, SIGMA, ZEISS microscope) and high-resolution transmission electron microscopy (TEM, TECNAI G20) were used to characterize the morphologies and structures of the as-prepared compounds. X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Escalab250Xi) were carried out with Al-K α as radiation source.

2.3. Electrochemical measurement

The electrochemical properties were tested through traditional slurry coating procedure. The slurry was consisted of 80 wt% cathode powders, 10 wt% carbon conductive agent and 10 wt% polyvinylidene fluoride (PVDF). Then, the slurry was coated on aluminum foil and dried for 24 h in a vacuum drying oven. The commercial electrolyte composed of 1 M LiPF_6 in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1: 1 in volume) was used. And the counter anode is a metallic lithium foil and a polypropylene micro-porous film was chosen as the separator. The coin-type cells (2016) were assembled in an argon-filled glove box in which H_2O and O_2 concentration were below 1 ppm. The galvanostatic discharge-charge tests were taken using a LAND battery program-control test system (Wuhan, China) at different charge-discharge current densities (20–2000 mA g^{-1}) in the voltage

Table 1
A comparison of different synthesis methods to obtain Li-rich oxides reported.

Author	Method	Time for precursor	Time for calcination	Total time
We	Full microwave synthesis	30 min	10 min	about 1 h
Y.K. Sun et al. [13]	Co-precipitation	12 h	20 h	>32 h
L.J. Zhang et al. [15]	Hydrothermal method	2–12 h	19–30 h	>21 h
E. Hosono et al. [17]	Electrospinning	3 h	3 h	>6 h
W.C. West et al. [19]	Solid state reaction	6 h	24 h	>30 h
C.S. Johnson et al. [21]	Co-precipitation	Not mentioned	6–11 h	>6 h
X.J. Guo et al. [22]	Co-precipitation	>4 h	13 h	>17 h
S.J. Shi et al. [23]	Freezing drying method	>2 days	12 h	>60 h
Y.J. Wei et al. [24]	Sol-gel method	>6 h	15 h	>21 h
J.M. Zheng [25]	Sol-gel method	Not mentioned	13 h	>13 h
S.H. Kang et al. [26]	Sol-gel method	Not mentioned	24 h	>24 h
P. Manikandan et al. [28]	Combustion synthesis	15 min	12 h	>12 h
S.J. Shi et al. [29]	Molten salt method	5 min	16 h	>16 h

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