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Synthesis of lithium nickel cobalt manganese oxide cathode materials by infrared induction heating

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HIGHLIGHTS

- An infrared sintering is adopted to synthesize $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (LNCM) powders.
- Crystalline LNCM powders are rapidly synthesized by the induction sintering method.
- The carbon coating onto LNCM is a crucial factor in facilitating cell performance.
- The C-coated LNCM cathode shows high capacity retention at 1*C* after 50 cycles.

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ABSTRACT

This study adopts an *in-situ* infrared (IR) sintering incorporated with carbonization technique to synthesize carbon-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (LNCM) cathode materials for Li-ion batteries. Compared with electric resistance heating, the *in-situ* IR sintering is capable of rapidly producing highly-crystalline LNCM powders at 900 °C within a short period, i.e., 3 h in this case. Glucose additive is employed to serve a carbon precursor, which is carbonized and coated over the surface of LNCM crystals during the IR sintering process. The electrochemical performance of LNCM cathodes is well examined by charge–discharge cycling at 0.1–5*C*. An appropriate carbon coating is capable of raising discharge capacity (i.e., 181.5 mAh g^{-1} at 0.1*C*), rate capability (i.e., 75.0 mAh g^{-1} at 5*C*), and cycling stability (i.e., capacity retention: 94.2% at 1*C* after 50 cycles) of LNCM cathodes. This enhanced performance can be ascribed to the carbon coating onto the external surface of LNCM powders, creating an outer circuit of charge-transfer pathway and preventing cathode corrosion from direct contact to the electrolyte. Accordingly, the *in-situ* IR sintering technique offers a potential feasibility for synthesizing cathode materials commercially in large scale.

1. Introduction

Lithium-ion battery is one of the most preferred power sources for portable electronic devices due to its high gravimetric and volumetric energy densities [1,2]. Up to now, one layered alkali transition metal oxide, $LiCoO_2$, has been in wide use as cathode materials, owing to its stability and high rate capability [3–5]. For example, Y.P. Fu group developed sol–gel technique to synthesize high-performance $LiCoO_2$ cathode materials [6]. They also used facile chemical method to prepare C-coated $LiCoO_2$ cathode in 2007 [7]. However, there is increasing demand for alternative materials to commercial $LiCoO_2$. The most challenging factor for $LiCoO_2$ cathode material is its expensive price because of the use of costly cobalt precursor. In order to reduce costly Co content, one multi-elemental cathode, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (LNCM), has received considerable attentions because of its high specific capacity, superior thermal stability, and lower Co-content making it more effective and less toxic [8,9]. Accordingly, pioneering studies have reported reliable synthesis of LNCM such as polymer template route [2], mixed hydroxide method [3], array transfer method [4], inverse micro-emulsion route [9], sol–gel method [8,10,11] and co-precipitation method [5,12]. More recently, our previous study also developed a chemical-wet synthesis incorporated with pulse microwave-assisted heating precursors and carbon coating technique to prepare highly-crystalline LNCM powders [13]. The LNCM cathodes are observed to show superior electrochemical performance, e.g., high specific capacity and cyclic stability. In traditional furnaces equipped with electric resistance heating systems, the sintering process is run at high temperatures between 600 and 900 °C, while make highly-crystalline LNCM grains. The sintering

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process usually takes a long heating period, ranging form 6–22 h. This drawback would cause higher electricity consumption and thus raise the production cost, which is not suitable for mass production.

To resolve the above problem, one strategy proposed here is to look for a low-cost synthesis method with short heating period. Recently, S. Uchida et al. employed a high-frequency induction heating incorporated with carbothermal reduction to synthesize C/$LiFePO_4$ composite in vacuum [14]. The induction heating technique allows the fast formation of olivine cathodes, opening a possibility to prepare cathode materials rapidly by induction heating. Herein the present work aims at fast synthesis of LNCM cathode using an induction heating infrared (IR) source. In fact, IR heating has been used extensively for surface coating, drying and curing of paints and coatings, moisture removal, and many practical applications [15]. Some researchers adopted the IR heating technique to sinter NiO buffer layer [16] and Ag nanoparticles on paper [17]. It is generally recognized that IR ray is an electromagnetic radiation with wavelength between visible light and microwave radiation [18]. Compared with traditional convective heating, the advantages of IR heater consist of (i) fast adsorber heat-up times, (ii) ability for programmable heating, (iii) controllability and (iv) high energy efficiency [15,19]. Besides, carbon coating is a crucial technique to improve the poor cyclic stability of LNCM cathodes, resulting from its low electronic conductivity, high reactivity between delithiated cathode and electrolyte, and serious dissolution of transition metal ions and electrolyte [20–22]. Hence, this study proposes an *in-situ* IR sintering combined with carbonization process to synthesize C/LNCM composites in a home-made induction oven, equipped with an IR heater array. Herein four LNCM cathodes with different carbon contents have been synthesized to explore their electrochemical performance, using charge–discharge measurement.

2. Experimental

The *in-situ* IR sintering incorporated with carbonization method was described as follows. First, the LNCM precursors, consisted of $CH_3COOLi \cdot 2H_2O$ (≥99.0%), $Ni(CH_3COO)_2 \cdot 4H_2O$ (≥98.0%), $Co(CH_3COO)_2 \cdot 4H_2O$ (≥99.5%), and $Mn(CH_3COO)_2 \cdot 4H_2O$ (≥99.0%), were dissolved in distilled water in a baker, forming a brownish metallic slurry. The stoichiometric ratio of metal ion solution was fixed at 3.3:1:1:1 in Li:Ni:Co:Mn, respectively. Here glucose ($C_6H_{12}O_6$) was chosen as carbon source, and the weight percentages of glucose in the LNCM precursors were set at 0.1, 0.25, 0.5, and 0.75%. The glucose solution was slowly added into the metallic slurry and then

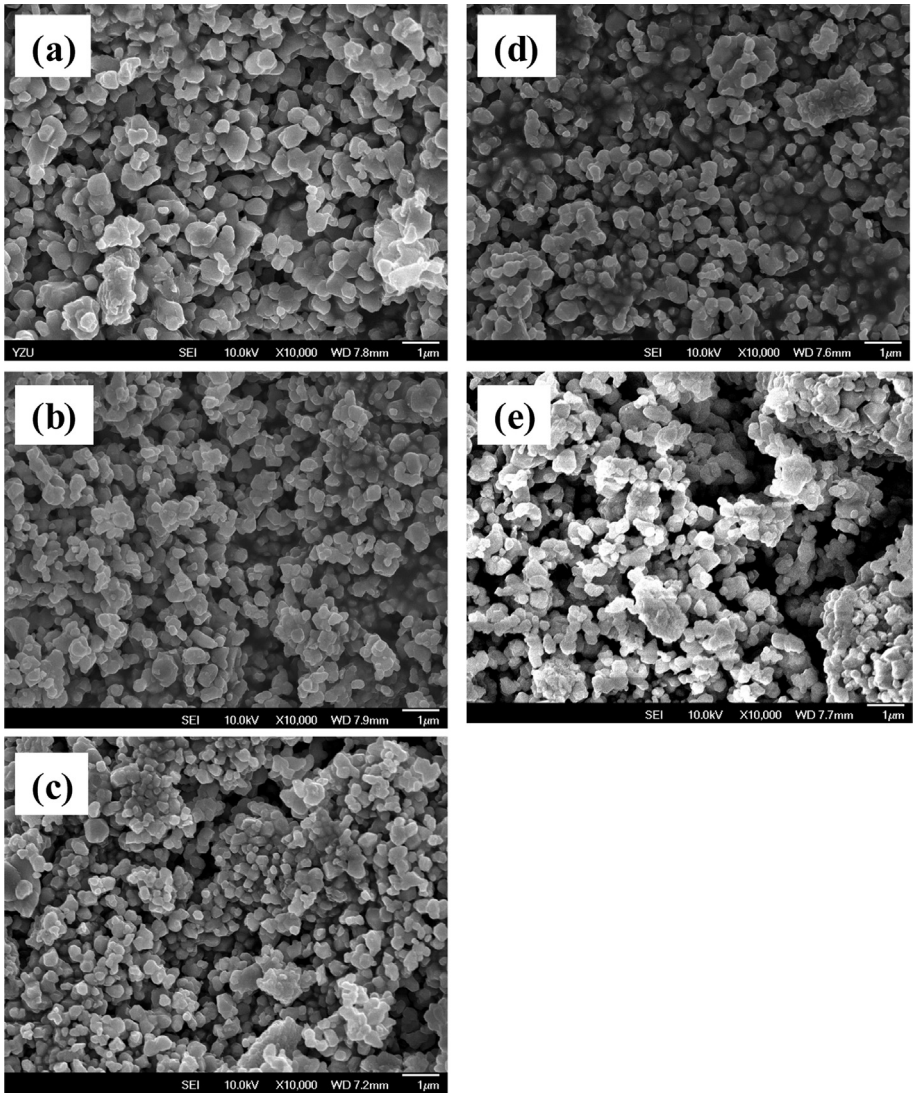

Fig. 1. FE-SEM images of (a) fresh LNCM, (b) LNCM-C1, (c) LNCM-C2, (d) LNCM-C3, and (e) LNCM-C4 powders.