



Infrared-assisted Synthesis of Lithium Nickel Cobalt Alumina Oxide Powders as Electrode Material for Lithium-ion Batteries



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ABSTRACT

This study explores an efficient infrared (IR) heating technique to synthesize highly-crystalline $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) cathode materials for Li-ion batteries. One home-made IR induction reactor, equipped with medium-wave IR emitter array, is adopted to prepare the NCA powders at 700 °C for a calcination period of 1–5 h. Two kinds of preparation routes, ball milling and rheological-phase method, are used to prepare NCA precursors. The as-prepared NCA powders display well ordering of hexagonal two-dimensional layer structure with low degree of cation mixing under appropriate conditions: IR heating time (5 h) and rheological-phase method. The NCA cathode exhibits an improved discharge capacity, fast Li^+ diffusion rate, high rate capability, and good cycling stability. This improved performance mainly originates from low cation mixing, low defect level, and homogeneous particle size of NCA crystals. The carbon-coated NCA cathode offers high capacities of ca. 213 and 115 mAh g^{-1} at 0.1 and 5C, respectively. Analyzed by the Randles-Sevcik plots, the diffusion coefficients in the NCA cathodes increase up to 1.73×10^{-8} and $5.82 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for Li-extraction and Li-insertion, respectively. Accordingly, the IR heating route turns on a commercial feasibility to synthesize NCA cathode materials for Li-ion battery application.

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1. Introduction

High energy density and power density of Li-ion batteries have made them a popular power source for portable electronic devices, and more recently, hybrid electric vehicles and plug-in hybrid electric vehicles [1–5]. It is generally recognized that Li-ion battery consists of four key components namely cathode, anode, polymeric separator, and electrolyte. Among the components, the selection of cathode materials plays the crucial role in determining the performance and the prime cost (~25%) of Li-ion batteries. Layered Ni-rich $\text{Li}(\text{Ni}_{1-x}\text{M}_x)\text{O}_2$ (M = transition metal, $x \leq 0.2$) cathode materials have been considered as a potential candidate for mobile tools and electric vehicles due to their low cost, low toxicity, and high specific capacity [6–8]. However, the Ni-rich $\text{Li}(\text{Ni}_{1-x}\text{M}_x)\text{O}_2$ was confirmed to exhibit low thermal stability, poor cycling behavior, and increased inner resistance, mainly originated from the structural instability [1,9]. The structural change can be attributed to the chemical uncertainty of Ni^{3+} and Ni^{4+} in layered

Ni-based lattices [10,11]. In alleviating the instability, Co and Al co-substituted $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) has been considered as one of the most applicable cathode materials in the Ni-rich $\text{Li}(\text{Ni}_{1-x}\text{M}_x)\text{O}_2$ family because of its improved thermal stability and enhanced electrochemical performance [10]. Pioneering studies also indicated that NCA could be a promising alternative to replace commercial LiCoO_2 cathode materials owing to its higher specific capacity and better environmental friendliness [12,13].

In spite of an improved performance, one of the challenges hindering commercial-scale application is finding a rapid and efficient synthesis route capable of producing NCA cathode materials. So far, several approaches to producing NCA have been studied, which include ball milling [6], co-precipitation crystallization method [1,12,14,15], sol-gel method [16], and molten-salt synthesis [17]. However, the NCA precursors should be generally calcined in oxygen-containing atmosphere with a temperature range of 600–850 °C for 8–24 h. Traditionally, the solid-state calcination was carried out in vertical or horizontal furnace, equipped with an electrical-resistive heating circuit. However, the electrical resistance furnaces are typically costly to maintain due to high energy consumption. Moreover, the conventional furnaces are usually inefficient (e.g., ramping rate: $1\text{--}10 \text{ }^\circ\text{C min}^{-1}$) in a number of respects often making the calcination process tedious and time

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consuming. This drawback would increase the electricity consumption and thus raise the production cost, which is not suitable for mass production [18]. Accordingly, one strategy for resolving the conventional heating problem is searching for an alternative heating system with high energy efficiency and high heating rate, which is appropriate for large-scale production of NCA cathode materials. More recently, Uchida group adopted a high-frequency induction heating incorporated with carbothermal reduction to prepare C-coated LiFePO₄ composite in vacuum [19]. In 2014, our group reported the *in-situ* infrared (IR) sintering technique, using carbon fiber heaters, to synthesize LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode materials within a short period of 3 h [18]. The induction heating techniques allow the rapid formation of crystalline powders, opening a feasibility towards preparing cathode materials efficiently by the induction heating.

Herein we develop an IR heating method to prepare highly-crystalline NCA powders by heating the precursors directly. The IR radiation can offer much faster and more uniform heating than traditional calcination methods [20]. It is well known that IR ray is an electromagnetic radiation with wavelength between visible light and microwave radiation [21]. The IR heating technique has been applied in a variety of practical applications such as thermal curing of polymers [22], sintering of NiO layers [23], nucleation of Ag nanocrystals [24], photo-thermal heating of confined water in polymer [25], and photo-induced reduction of thermoplastic composites [26]. One home-made IR reactor with six heaters was assembled for calcining two kinds of NCA precursors, made from ball milling and rheological-phase method. The IR reactor could be operated at a fast heating rate of 100 °C min⁻¹, which is ten times higher than that of traditional furnaces. The influence of calcination time on the electrochemical performance of two sets of NCA powders was systematically investigated. The work would shed some lights on how the synthesis method and calcination period affect the electrochemical performance of NCA cathodes. On the basis of the experimental results, the IR heating technique can be regarded as the most effective method for the synthesis of NCA cathodes due to its potential for short NCA heat-up time, high energy efficiency, and certain ability in programmable heating.

2. Experimental

Two sets of NCA precursors were prepared, one by ball milling and another by rheological-phase method. As to the ball milling, one solid mixture containing LiOH·H₂O, Ni(OH)₂, Co(OH)₂, and Al(OH)₃ was uniformly dispersed in ethanol solution. The stoichiometry ratio of Ni:Co:Al was set at 80:15:5. The mixture was blended and milled by a three-dimensional mixer using Zr balls for 6 h. Two types of Zr balls (i.e., diameter: 3 and 10 mm) were used as mill and the weight ratio of NCA precursor to Zr balls was fixed at 1:10. After ball milling, the solid mixture was put into the IR induction reactors, which was equipped with six medium-wave IR heater with near-IR wavelength region of 1.4–3.2 μm. Each IR filament had a maximum surface power of 80 kW m⁻². The heaters consisted of metallic filament and quartz tube as cover. The near-IR heaters were capable of transferring energy to a body through electromagnetic radiation, i.e., no contact or medium between the two bodies for the energy transfer [18]. The IR calcination process was performed by heating the mixture from room temperature to 700 °C in air with a ramping rate of 100 °C min⁻¹ and keeping this temperature for 1, 3, and 5 h. After cooling down to ambient temperature, the solid samples were sieved through a stainless foil mesh (Type: 300 mesh). The NCA samples were designated as M1, M2, and M3, according to different IR heating periods of 1, 3, and 5 h, respectively.

As for the rheological-phase method, one mixture containing LiOH·H₂O, Ni(OH)₂, Co(OH)₂, and Al(OH)₃ was uniformly dispersed

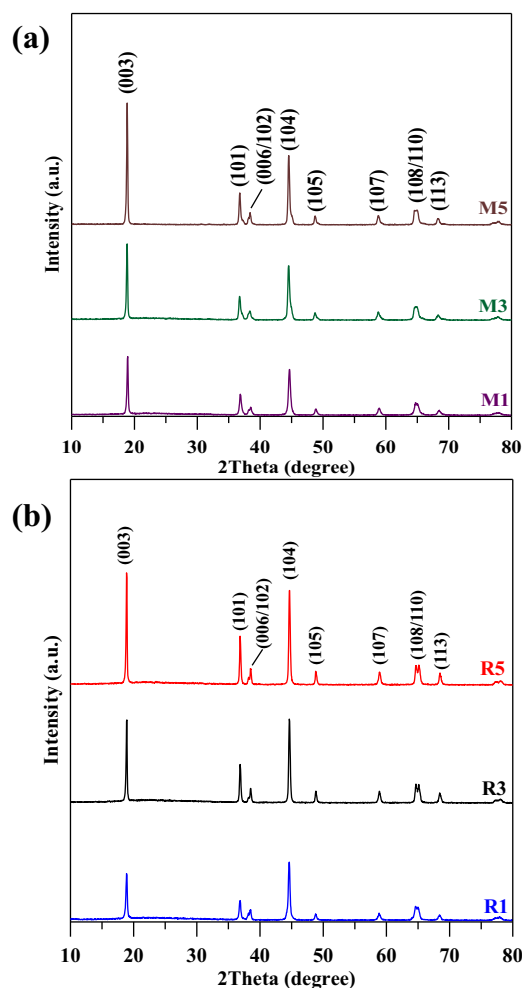


Fig. 1. Typical XRD patterns of different NCA powders prepared by the IR heating technique: (a) M and (b) R sample series.

in ammonia water (500 mL) through a vigorous stirring process. The molar ratio of Ni:Co:Al was fixed at 80:15:5. The slurry was then heated to 70 °C and maintained at this temperature for 6 h. The rheological-phase process was continuously stirred with a rotation speed of 130 rpm. The sample was placed into a vacuum oven and dried at 120 °C for 6 h, ensuring the complete removal of moisture. In the home-made IR reactor, we equipped three K-type thermocouples (Maximum Electronic Co.) to detect in the real temperature of test sample and IR heaters. The distance between the top of thermocouple and the NCA precursor was set at 0.5 cm. For accuracy, the distance between the sample and the thermocouple was adjusted for each experimental run. The NCA precursor was carefully put into alumina crucible. The IR calcination process was carried out by heating the sample at 700 °C in air for 1, 3, and

Table 1
Lattice parameters and atomic compositions of all NCA samples.

Sample	<i>c/a</i>	Unit cell volume (Å ³)	<i>I</i> ₀₀₃ / <i>I</i> ₁₀₄	R-factor	Ni:Co:Al
M1	4.91	99.8	1.3	0.58	79.1:15.0:5.9
M3	4.92	100.9	1.4	0.56	79.5:14.8:5.7
M5	4.92	100.6	1.7	0.52	79.2:14.5:6.3
R1	4.93	99.8	0.8	0.96	80.0:15.1:4.9
R3	4.88	100.0	1.0	0.57	80.1:15.0:4.9
R5	4.93	101.0	1.2	0.52	80.1:15.2:4.7
T5	4.89	100.2	1.0	0.60	78.8:15.1:6.1

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