



# Synthesis of a Co–Ni doped $\text{LiMn}_2\text{O}_4$ spinel cathode material for high-power Li-ion batteries by a sol–gel mediated solid-state route



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## ABSTRACT

A Co–Ni doped  $\text{LiMn}_2\text{O}_4$  spinel cathode material with a nominal stoichiometry of  $\text{LiMn}_{1.95}\text{Co}_{0.025}\text{Ni}_{0.025}\text{O}_4$  was synthesized by a sol–gel mediated solid-state route at a low temperature of 650 °C, using a highly dispersed ultra-fine  $\text{Mn}_2\text{O}_3$  as the Mn source. Also, a pelletizing process was adopted to optimize its morphology. It was revealed that the Co–Ni doped  $\text{LiMn}_2\text{O}_4$  obtained consisted of porous nanoparticles-constructed  $\text{LiMn}_{1.95}\text{Co}_{0.025}\text{Ni}_{0.025}\text{O}_4$  granules with a size of 30–50  $\mu\text{m}$ , which combined the favorable characteristics of both nano-sized and bulk materials, i.e. considerably large specific surface area and high tap density. The cathode material exhibited excellent electrochemical performance. Notably, its rate capability was extraordinarily high, which was superior to that of pristine or doped  $\text{LiMn}_2\text{O}_4$  materials ever reported. It showed a discharge capacity of 119  $\text{mA h g}^{-1}$  at a current rate of 0.2 C (1 C = 148  $\text{mA g}^{-1}$ ), and retained a capacity of 111  $\text{mA h g}^{-1}$  at 10 C, presenting a 93% capacity retention. After 200 cycles at 1 C and 25 °C, it delivered a capacity of 112  $\text{mA h g}^{-1}$ , retaining 97% of its initial capacity. After 100 cycles at 1 C and 55 °C, it showed a capacity of 110  $\text{mA h g}^{-1}$ , preserving 96% of its initial capacity. The excellent electrochemical performance together with the facile synthesis process allowed the synthesized  $\text{LiMn}_{1.95}\text{Co}_{0.025}\text{Ni}_{0.025}\text{O}_4$  to be a promising cathode material for high-power Li-ion batteries.

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## 1. Introduction

Spinel  $\text{LiMn}_2\text{O}_4$  has been recognized as a promising cathode material for Li-ion batteries, due to its proper  $\text{Mn}^{3+}/\text{Mn}^{4+}$  redox potential (4 V vs.  $\text{Li}/\text{Li}^+$ ), low cost, environmental benignity and high safety [1–3]. However, it suffers from severe capacity fading after cycling or storage, especially at elevated temperatures [4]. Various mechanisms have been proposed to explain the capacity fading, including dissolution of Mn cations into electrolyte, Jahn–Teller distortion, and changes in crystallinity [5–7]. It was found that doping of metal ions, such as Al [8], Ni [9], Co [10], Cr [11] and Ti [12] ions, into  $\text{LiMn}_2\text{O}_4$  spinel can enhance its structural stability, consequently its cyclability can be apparently improved. Nevertheless, in most cases, the cyclability improvement is accompanied by a remarkable decline in specific capacity, because of the replacement of the partial active Mn ions by the inactive metal ions

[8,9,11,12]. As a result, great efforts have been devoted to the exploration of facile synthesis methods for achieving doped  $\text{LiMn}_2\text{O}_4$  cathode materials with satisfactory electrochemical performance.

Nowadays, the methods for synthesis of single- or multi-cation doped  $\text{LiMn}_2\text{O}_4$  can be grouped into solid-state route [8,12,13] and wet-chemical route [9–11,14–19]. The solid-state route is most frequently used, which involves mixing and milling of lithium hydroxide or lithium carbonate, manganese dioxide, and metal oxide dopants at room temperature, and calcining the milled precursors at elevated temperatures during which spinel structure is formed. Though facile and low-cost, this method requires a relatively high calcining temperature, usually above 800 °C, for obtaining single-phase spinel compounds, due to insufficient chemical homogeneity of the milled precursors. The elevated calcining temperatures applied incur not only the coarsening of crystallites but also the formation of oxygen vacancies in spinel lattice [20]. As a result, electrochemical performance, especially specific capacity and cyclability, of the resulting doped  $\text{LiMn}_2\text{O}_4$  materials is not so satisfactory. The wet-chemical route mainly includes sol–gel processes [14,15], coprecipitation processes [18], and other

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modified sol–gel or coprecipitation processes [10,11,17,19]. Generally, the precursors synthesized by the wet-chemical route show higher chemical homogeneity. As a result, single-phase doped  $\text{LiMn}_2\text{O}_4$  materials, usually composed of nano-sized particles, can be synthesized at lowered calcination temperatures. Nevertheless, due to a higher ratio of organic ingredients required, and/or more and complicated processing steps involved, the wet-chemical route are often less efficient and higher cost. Therefore, from a practical point of view, the wet-chemical route is not the ideal one for large-scale synthesis of doped  $\text{LiMn}_2\text{O}_4$  cathode materials.

In this work, a porous nanoparticles-constructed  $\text{LiMn}_{1.95}\text{Co}_{0.025}\text{Ni}_{0.025}\text{O}_4$  cathode material was achieved by a sol–gel mediated solid-state route combined with a pelletizing process, using highly dispersed ultra-fine  $\text{Mn}_3\text{O}_4$  as Mn source. The sol–gel mediated solid-state route combines the advantages of sol–gel method and solid-state method. The synthesis method is highly efficient and low cost, requiring a small ratio of organic ingredients, and allowing the synthesis temperature to be lowered to as low as  $650^\circ\text{C}$ . Furthermore, the resulting  $\text{LiMn}_{1.95}\text{Co}_{0.025}\text{Ni}_{0.025}\text{O}_4$  cathode material presents a favorable morphology of porous nanoparticles-constructed granules, which have the advantages of nano-sized and bulk materials, i.e. large specific surface area and high tap density. The  $\text{LiMn}_{1.95}\text{Co}_{0.025}\text{Ni}_{0.025}\text{O}_4$  cathode material shows excellent cyclability and extraordinarily good rate capability. More importantly, its specific capacity is not compromised, still as large as  $119\text{ mA h g}^{-1}$ . To the best of our knowledge, the relative investigations have not been reported. Our work provides a facile and efficient approach to synthesis of single- or multi-cation doped  $\text{LiMn}_2\text{O}_4$  cathode materials with high electrochemical performance. It is demonstrated that the obtained  $\text{LiMn}_{1.95}\text{Co}_{0.025}\text{Ni}_{0.025}\text{O}_4$  is a promising cathode material for high-power Li-ion batteries.

## 2. Experimental

### 2.1. Material synthesis

The Co–Ni doped  $\text{LiMn}_2\text{O}_4$  spinel cathode material, whose nominal chemical compositions were designed to be  $\text{LiMn}_{1.95}\text{Co}_{0.025}\text{Ni}_{0.025}\text{O}_4$ , was synthesized by a sol–gel mediated solid-state method. A highly dispersed  $\text{Mn}_3\text{O}_4$  powder was used as the Mn source, which possessed a particle size of  $\sim 150\text{ nm}$  and a specific surface area of  $14.3\text{ m}^2\text{ g}^{-1}$ . It was synthesized by a precipitation–oxidation method, which was described in detail in our previous work [21]. All the other reagents were of analytical grade, provided by Sinopharm Chemical Reagent Co. Ltd., and used as received. In a typical experiment,  $63\text{ mmol}$  ( $13.2388\text{ g}$ ) of citric acid monohydrate ( $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ ) was dissolved in  $400\text{ mL}$  deionized water, and  $200\text{ mmol}$  ( $8.3928\text{ g}$ ) of lithium hydroxide monohydrate ( $\text{LiOH}\cdot\text{H}_2\text{O}$ ),  $5\text{ mmol}$  ( $1.4452\text{ g}$ ) of cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ) and  $5\text{ mmol}$  ( $1.4540\text{ g}$ ) of nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ) were dissolved in deionized water, respectively. The lithium hydroxide solution was added into the citric acid solution, adjusting its pH value to  $\sim 6$  with nitric acid and aqueous ammonia. The cobalt nitrate and nickel nitrate solutions were added to the above citric acid solution. The obtained solution was energetically stirred and evaporated at  $70^\circ\text{C}$  for  $2\text{ h}$ , during which,  $25.2\text{ mmol}$  ( $1.5642\text{ g}$ ) of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) was added to promote the formation of gelatin. The wet gelatin was mixed with  $130\text{ mmol}$  ( $29.7454\text{ g}$ ) of  $\text{Mn}_3\text{O}_4$ , and ball-milled for  $3\text{ h}$ , using a planetary mill. The milled mixture was dried at  $120^\circ\text{C}$ , and preheated at  $450^\circ\text{C}$  for  $5\text{ h}$ , yielding a preheated precursor. A half of the preheated precursor was directly calcined in air at  $650^\circ\text{C}$  for  $10\text{ h}$ , resulting in a Co–Ni doped  $\text{LiMn}_2\text{O}_4$  sample called the agglomerate-LMCNO. The other half was ball-milled for  $3\text{ h}$ , and fully mixed with a proper amount of polyvinyl alcohol solution, and pressed into cylindrical pellets at a  $10\text{ t}$  load for  $5\text{ min}$ . The obtained pellets were crushed and ground into granules with a size of  $30\text{--}50\text{ }\mu\text{m}$ . The prepared granules were calcined in air at  $650^\circ\text{C}$  for  $10\text{ h}$ , yielding a Co–Ni doped  $\text{LiMn}_2\text{O}_4$  sample called the granule-LMCNO.

### 2.2. Structural and electrochemical characterization

Phase compositions of the obtained Co–Ni doped  $\text{LiMn}_2\text{O}_4$  samples were analyzed by using a Philips X'pert Pro X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406\text{ \AA}$ ). Diffraction data were collected in the  $2\theta$  range from  $10^\circ$  to  $80^\circ$ , using the step-scan mode with a scanning speed of  $0.02^\circ$  step size and  $1\text{ s}$  per step. For determining the chemical composition of the obtained samples, element analysis

for Li, Mn, Co and Ni was carried out using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Model Atomscan Advantage spectrometer. Their morphology and structure were analyzed by a field emission scanning electron microscope (FESEM) of Nano SEM 430, and a transmission electron microscope (TEM) of JEM-2100 at an acceleration voltage of  $200\text{ kV}$ . Nitrogen adsorption–desorption measurements were performed at a Coulter SA3100 system at  $77.3\text{ K}$ . The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. Tap density of the obtained samples was determined by the following method:  $\sim 9\text{ g}$  of the sample was weighed, and placed in a  $10\text{-mL}$  glass measuring cylinder, and then the cylinder was lifted to a height of  $10\text{ cm}$  and dropped onto a  $2\text{-cm}$  thick rubber board for  $200$  times. The tap density was calculated according to the mass and the final volume of the sample.

To evaluate electrochemical performance, coin cells with CR2025 configuration were assembled in an argon-filled glove box, using lithium foil as the anode, Celgard 2400 polypropylene membrane as the separator,  $1\text{ mol L}^{-1}$   $\text{LiPF}_6$  in a 50:50 (in volume ratio) mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) as the electrolyte, and the synthesized Co–Ni doped  $\text{LiMn}_2\text{O}_4$  as the cathode active material. The cathode mix slurry consisted of the active material, acetylene black and polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP) solvent in a weight ratio of 80:10:10. The slurry was coated over aluminium foil, and vacuum-dried at  $110^\circ\text{C}$  for  $10\text{ h}$ . The dried coating was pressed under a  $2\text{ t}$  load for  $1\text{ min}$ , and electrodes with a diameter of  $16\text{ mm}$  were punched out. The cells were galvanostatically cycled between  $3.4$  and  $4.3\text{ V}$  vs.  $\text{Li/Li}^+$  using a battery test system of Neware BST-3008 W. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on a CHI660C electrochemistry workstation in a three-electrode cell set-up, using a synthesized active material electrode as the working electrode, a lithium foil as the counter electrode and the reference electrode. CV curves at various scan rates of  $0.1\text{--}0.5\text{ mV s}^{-1}$  were recorded in the potential range of  $3.4\text{--}4.4\text{ V}$  vs.  $\text{Li/Li}^+$ . EIS spectra were measured applying an a.c. amplitude of  $5\text{ mV}$  in a frequency range of  $10^5\text{--}10^{-2}\text{ Hz}$ . Before the EIS measurements, both the cell samples were subjected to an initial charge–discharge cycle, then charged to  $4.1\text{ V}$  vs.  $\text{Li/Li}^+$ . The measured EIS spectra were fitted using ZSimpWin software.

## 3. Results and discussions

### 3.1. Structural characterization

XRD patterns of the agglomerate- and granule-LMCNO samples are given in Fig. 1(a) and (b), respectively. The sharp and strong diffraction peaks indicate that both the samples are well crystallized. Apparently, the XRD patterns can be indexed based on a cubic spinel  $\text{LiMn}_2\text{O}_4$  (JCPDS card no. 35-0782) with the space group of  $\text{Fd}\bar{3}\text{m}$ , where the Li and Mn cations occupy the  $8\text{a}$  tetrahedral and  $16\text{d}$  octahedral sites of the cubic close-packed oxygen anions framework, respectively. Also, it is clearly demonstrated that both the samples are spinel-structured without other impurities formed. The formation of the single-phase Co–Ni doped  $\text{LiMn}_2\text{O}_4$  spinel at a relatively low temperature of  $650^\circ\text{C}$  might be associated with the sol–gel mediated solid-state route adopted. In the sol–gel process, the Li, Co and Ni cations were initially anchored on the citric acid molecules, consequently,

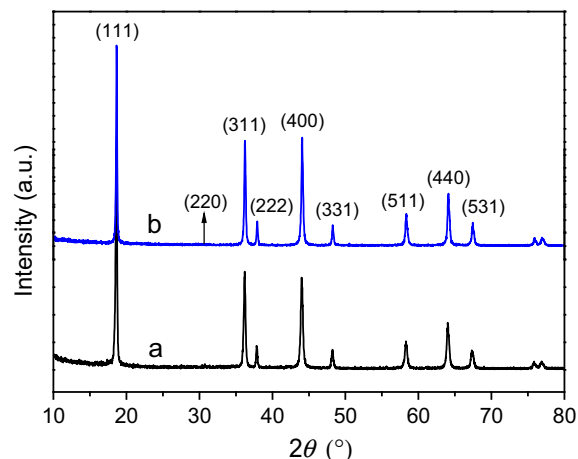


Fig. 1. XRD patterns of the (a) agglomerate- and (b) granule-LMCNO samples.

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