



# Magnesium and silicon co-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material with outstanding cycling stability for lithium-ion batteries



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## ABSTRACT

The magnesium (Mg) and silicon (Si) co-doped  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  sample has been obtained by sol-gel method. The effects of co-doping with magnesium and silicon ions on the phase structure, morphology and electrochemistry characteristics of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  are investigated by a series of physico-chemical characterizations. XRD results demonstrate that the magnesium and silicon ions successfully enter into the spinel structure and make the lattice parameter slightly increased. Moreover, the magnesium and silicon ions co-doped sample presents superior cycling stability. When cycled at 0.5 C, this sample still delivers  $121 \text{ mAh g}^{-1}$  after 100 cycles with outstanding retention of 98.86%, while the undoped  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  sample only exhibits  $104.5 \text{ mAh g}^{-1}$  after 100 cycles with low retention of 79.17%. In addition, the  $\text{Mg}^{2+}$  and  $\text{Si}^{4+}$  co-doped sample shows outstanding rate capability and low charge transfer resistance.

## 1. Introduction

The research of lithium-ion batteries (LIB) is of great concern for power source applied to EV, HEV and energy storage systems [1,2]. As an important part of LIB, the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  has been seen as one promising high-voltage cathode material due to its relatively inexpensive price, abundant raw materials, and high energy density ( $650 \text{ Wh/kg}$ ) because of the high voltage platform ( $\sim 4.7 \text{ V}$  vs  $\text{Li}^+/\text{Li}$ , corresponding with  $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$  redox reaction) [3,4]. Moreover, the three-dimensional channels structure for  $\text{Li}^+$  diffusion makes  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  has high intrinsic rate capacity [5,6]. However, it is important to note that the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is vulnerable to a bad interaction with electrolyte at high charge-discharge voltage, especially under the condition of elevated temperature, which results in the rapid capacity fade during cycling [7,8]. These serious problems severely constrain the large-scale industrial application of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ .

To design this material towards superior electrochemical performances, a mass of modification strategies have been implemented, including various synthesis routes (such as microwave-assisted sol-gel [9,10], co-precipitation [11], ultrasonic spray pyrolysis [12], hydrothermal [13], low-temperature solution combustion [14,15], solid-state

reaction [16]), special morphology (hollow microsphere structures [17], nanofiber shape [18], polyhedral structure [19]), substitution and surface modification [20–23]. Among these modification strategies, replacing Ni or (and) Mn site with other cations, such as  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Si}^{4+}$  and some rare earth element ions [24–28], is confirmed to play a positive role in stabilizing structure and enhance electrochemical properties. Some research results show that  $\text{Mg}^{2+}$  doping can optimize the electronic conductivity, which can help to enhance the electrochemical properties [29]. Moreover, F. G. B. Ooms et al. [30] have found that the introduction of Mg ions can stabilize the material structure of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and decrease the impurity phase of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ . However, it is significant to realize that the substitution Ni sites with inactive  $\text{Mg}^{2+}$  to excess can engender adverse effect on the discharge capacity due to the reduction of active  $\text{Ni}^{2+}$ . To reduce the substitution of Ni sites, some tetravalent cations such as  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$  are used to substitute Mn sites [31,32].  $\text{Si}^{4+}$  doping in spinel structure is also a good method to improve the electrochemical performances, which has been reported by several theses [33–35]. It might be attributed to the stronger bond energy for Si–O compared with Ni–O and Mn–O [36]. In addition, Si is an abundant, low-cost and nontoxic element.

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In this work, we firstly propose the  $Mg^{2+}$  and  $Si^{4+}$  co-doping strategy to optimize the electrochemical performance of  $LiNi_{0.5}Mn_{1.5}O_4$ . The  $Mg^{2+}$  and  $Si^{4+}$  co-doped material was successfully obtained by sol-gel technology. The material structure, surface morphology and electrochemical performance were characterized by XRD, FTIR, FESEM, galvanostatic charge-discharge test and EIS. As expected, the  $Mg^{2+}$  and  $Si^{4+}$  co-doped sample showed outstanding cycling life and rate capability due to the synergistic effect of co-doping with magnesium and silicon ions on the  $LiNi_{0.5}Mn_{1.5}O_4$  cathod material.

## 2. Experimental

### 2.1. Synthesis

The  $Mg^{2+}$  and  $Si^{4+}$  co-doped sample ( $LiNi_{0.47}Mg_{0.03}Mn_{1.47}Si_{0.03}O_4$ , denoted as  $Mg_{0.03}Si_{0.03}$  in figures) was obtained by sol-gel method. That includes the following steps: the mixed solution A was prepared by dissolving a moderate amount of citric acid and lithium hydroxide in deionized water. The mixed solution B was prepared by dissolving nickel acetate, manganese acetate and magnesium nitrate in deionized water. Then, the mixed solution B and ethanol solution of TEOS were added dropwise into the mixed solution A. The ammonia solution was used to adjust the pH value to 7.0. The homogeneous mixed solution was evaporated at  $80^\circ C$  under stirring in the water bath to form a wet gel. The wet gel was firstly dried at  $110^\circ C$  for 24 h in air. Finally, the dried gel was calcined at  $450^\circ C$  for 4 h in muffle furnace. After being ground, the precursor powder was sintered at  $800^\circ C$  and followed by an annealing process. The flow chart was shown in Fig. 1. The undoped material ( $LiNi_{0.5}Mn_{1.5}O_4$ , denoted as LNMO in figures) was synthesized by the same method.

### 2.2. Characterization

The crystalline phase was identified by the X-ray diffraction (XRD, DX-1000 CSC; Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The scanning angle of  $2\theta$  varies from  $10^\circ$  to  $120^\circ$  and with a step of  $0.013^\circ$ . To distinguish the two space groups of prepared materials, the Fourier transform infrared spectroscopy (FTIR) was performed by a SHIMADZU FTIR-8400s spectrophotometer (the wave number range is  $700\text{--}400 \text{ cm}^{-1}$ ,  $\phi 13$  pellets). The surface morphologies of the prepared samples were studied by scanning electron microscopy (FESEM, INSPECT-F). The energy dispersive spectrometer (EDS) was used to examine the element composition.

### 2.3. Electrochemical test

The cathode electrode contained the obtained active material (85 wt%), acetylene black (10 wt%) and binder (5 wt%, PVDF dissolved in N-methyl-2-pyrrolidone (NMP)). The mixed slurry was coated on the Al foil and dried at  $105^\circ C$  for 4 h in air. The CR2025 coin-type batteries

were prepared by using electrolyte which was obtained by dissolving 1 M  $LiPF_6$  in the mixed solution of dimethyl carbonate (DMC), ethylmethyl carbonate (EMC) and ethylene carbonate (EC) (EMC: EC: DMC = 1: 1: 1 v/v/v). The galvanostatic charge-discharge test including cycle and rate performance were done on Land Battery Testing System (Land CT2001A). The electrochemical impedance spectroscopy (EIS) were tested on the electrochemical workstation (Correst CS-350, 5 mV alternative current signal amplitude, 0.01 Hz-100 kHz).

## 3. Results and discussion

### 3.1. Structural and morphological analyses

In general, the spinel  $LiNi_{0.5}Mn_{1.5}O_4$  possesses two kinds of Fd-3m and  $P4_332$  according to the Ni/Mn arrangement [37]. The Fd-3m space group corresponds with a nonstoichiometric and disordered structure, in which Ni and Mn randomly occupy the octahedral sites (16 d), and O occupy 32e sites. Besides, there are some  $Mn^{3+}$  ions within this Fd-3m structure that attributes to the oxygen deficiency result from the high temperature sintering process [38]. The  $P4_332$  space group corresponds with a stoichiometric and ordered structure, in which Ni and Mn occupy the 4 b and 12 d sites, respectively, and O occupy 8c and 24e sites. The Fd-3m and  $P4_332$  structure correspond with two different JCPDS cards of No. 80-2162 and No.80-2184, respectively. Moreover, two of the space groups can be distinguished by FTIR or Raman spectrum.

The XRD results of the undoped  $LiNi_{0.5}Mn_{1.5}O_4$  and  $LiNi_{0.47}Mg_{0.03}Mn_{1.47}Si_{0.03}O_4$  samples are shown in Fig. 2. These two materials are confirmed to have well-crystallized spinel structure as all the characteristic diffraction peaks match pretty well with the standard JCPDS card of No.80-2162, indicating that the magnesium and silicon ions doesn't alter the pristine spinel structure of this material. Furthermore, the partial enlarged drawing of (111) peak presents a slight movement to smaller angle for the Mg–Si co-doped sample, which indirectly interprets the successful introduction of magnesium and silicon ions and an increase of the unit cell volume of the co-doped sample. The average crystalline size of prepared materials can be calculated by the Debye-Scherrer equation ( $D = K\lambda/B\cos\theta$ ) based on the strongest (111) peak. The average crystalline size of un-doped and co-doped material are 73.95 nm and 71.01 nm, respectively. Apparently, the Mg–Si co-doping decrease the average crystalline size of  $LiNi_{0.5}Mn_{1.5}O_4$  material. It is generally known that the (220) diffraction peak at about  $2\theta = 31^\circ$  is related to the electron density on the 8a tetrahedral site in the spinel structure. The intensity of (220) diffraction peak is usually very weak due to the fact that only  $Li^+$  ions are located at 8a tetrahedral site, but its intensity increases when ions with higher electron density occupy the tetrahedral site [5]. From Fig. 2, we can see there is no obvious diffraction peak around  $2\theta = 31^\circ$  of the two prepared materials, the nearly ignorable intensity of (220) diffraction peak suggests that the tetrahedral 8a sites aren't occupied by transition metal ions and  $Mg^{2+}/Si^{4+}$  [5,33]. The weak peak at about  $2\theta = 43.6^\circ$  is identified as  $Li_xNi_{1-x}$ .

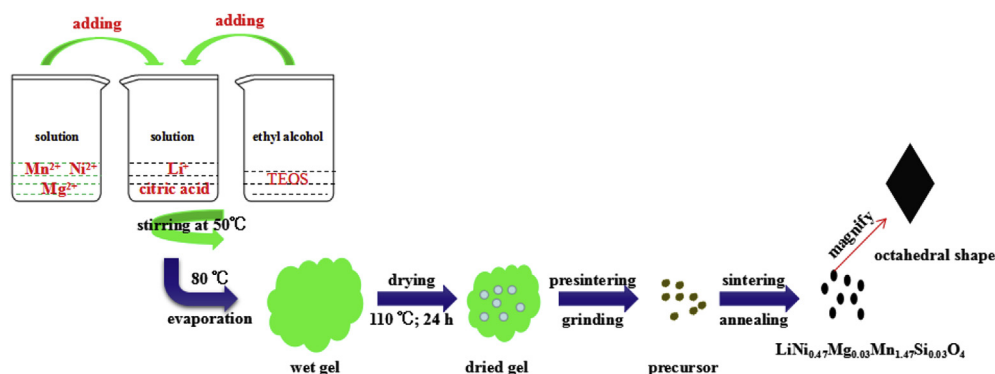


Fig. 1. Synthetic process flow chart of  $LiNi_{0.47}Mg_{0.03}Mn_{1.47}Si_{0.03}O_4$ .

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