



# A superior $\text{Li}_2\text{SiO}_3$ -Composited $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode for High-Voltage and High-Performance Lithium-ion Batteries



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## ABSTRACT

In this work,  $\text{Li}_2\text{SiO}_3$ , a layer-structured fast  $\text{Li}^+$ -ion conductor with three-dimensional  $\text{Li}^+$  paths, has been firstly introduced into  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  to form novel cathode composites of  $(1-x)\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \cdot x\text{Li}_2\text{SiO}_3$  via a citric acid-assisted sol-gel method. The effects of  $\text{Li}_2\text{SiO}_3$  on the phase structure, morphology and electrochemical performance of the materials were investigated. As  $x$  increases, the structure and electrochemical properties of the materials are tailored. The cathode material with  $x=0.10$  delivers ultrahigh initial discharge capacity  $\sim 150.3 \text{ mAh g}^{-1}$ , which is 24.4% larger than that of the pristine  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  ( $120.8 \text{ mAh g}^{-1}$ ). The  $\text{Li}_2\text{SiO}_3$ -composited  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  materials present an enhanced cycling stability, better rate performance and lower charge transfer resistance. These excellent electrochemical properties indicate that the compositing of fast  $\text{Li}^+$ -ion conductor  $\text{Li}_2\text{SiO}_3$  is an effective method to enhance the electrochemical performance of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ -based cathode materials.

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## 1. Introduction

Lithium-ion batteries have been extensively studied and used as power sources, due to their high power and energy density [1–5]. To achieve the higher energy density and good safety of lithium-ion batteries, the high-voltage spinel cathode materials of  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  ( $M = \text{Co}, \text{Ni}$ ) have been extensively studied [6,7]. Thus, it is the urgent need to fabricate new cathode materials for LIBs with high energy density and high capacity [8–12]. Among these spinel cathode materials,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  has attracted great attention owing to its very high operating voltage of about 4.7 V and low cost [11–14]. However, the practical application of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  has been limited because of its low discharge capacity (theoretical capacity  $\sim 147 \text{ mAh g}^{-1}$ ) and fast fading of capacity upon prolonged cycling. These drawbacks of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  are mainly caused by the following factors: (1) the inherently slow ion diffusivity and low electronic conductivity [15–17]; (2) the Jahn-Teller distortion caused by  $\text{Mn}^{3+}$  during the charge-discharge process [18]; (3) the formation of oxygen vacancies at high temperature [19]; and (4) the dissolution of Mn ions via a chemical reaction:  $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$  at high

working potential [6]. Many investigations have been carried out to overcome these shortcomings, such as the doping of metal ion (e.g., Cr, Ru, Cu or V, etc) [20–23], surface coating (e.g.,  $\text{Al}_2\text{O}_3$ , CuO,  $\text{SiO}_2$ , ZnO,  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_2\text{CO}_3$ , etc) [24–29] and so on. For examples, R. Verrelli et al. have synthesized Cu-doped spinel cathode material (i.e.,  $\text{Li}_{0.85}\text{Ni}_{0.46}\text{Cu}_{0.1}\text{Mn}_{1.49}\text{O}_4$ ) by a solid state process and the sample exhibited a discharge capacity of  $\sim 100 \text{ mAh g}^{-1}$  at 0.1 C [22]; W. K. Shin et al. reported that the coating of  $\text{SiO}_2$  improves the electrochemical performance of spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , and the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4@3\text{wt}\%\text{SiO}_2$  electrode delivered a high discharge capacity of  $130.7 \text{ mAh g}^{-1}$  at 0.1 C [26]. Recently, the spinel materials coated with fast  $\text{Li}^+$ -ion conductors (e.g.,  $\text{Li}_2\text{CO}_3$ ,  $\text{LiPO}_3$ ,  $\text{Li}_2\text{TiO}_3$ , etc) have been frequently studied, giving enhanced electrochemical performance (discharge capacities of  $\sim 135 \text{ mAh g}^{-1}$ ) [29–33]. It should be noted that although the surface coating of fast  $\text{Li}^+$ -ion conductor, to some extent, is effective to heighten the cyclic performance and rate capability of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode, it still cannot meet the requirements of the practical applications. Most of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ -based materials still exhibit relative low discharge capacities of  $\sim 100\text{--}130 \text{ mAh g}^{-1}$  [11–14,18,19]. Therefore, it is very important to develop a feasible approach to further improve the electrochemical performance of the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ -based cathodes.

Recently,  $\text{Li}_2\text{SiO}_3$ , a novel and typical  $\text{Li}^+$ -ion conductor, has been widely studied as a surface modifier for cathode materials

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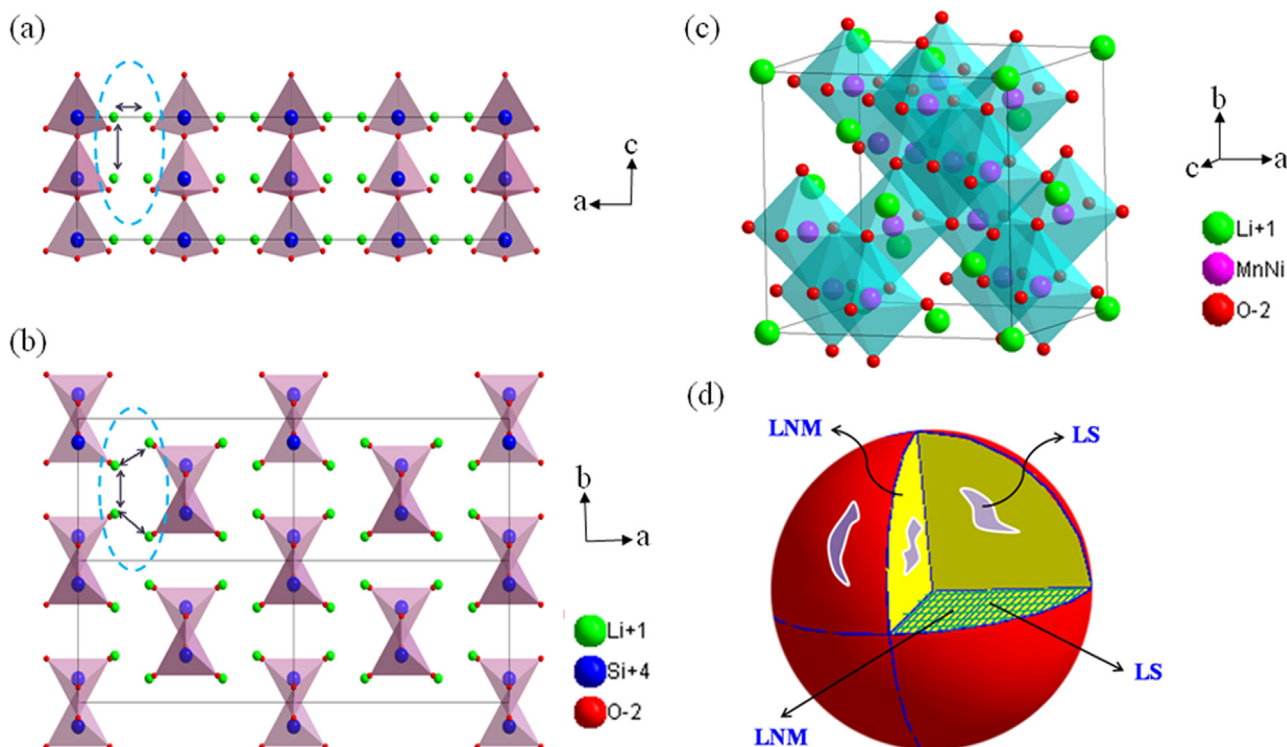
[34–36]. For example, Gao et al. prepared a  $\text{Li}_2\text{SiO}_3$ -coated lithium-rich  $\text{Li}_{1.8}[\text{Mn}_{0.7}\text{Co}_{0.15}\text{Ni}_{0.15}]\text{O}_{2.675}$  cathode material, and their investigation show that the coating of 1.5 wt%  $\text{Li}_2\text{SiO}_3$  effectively improved the rate capability and cycling performance of the material [36]; Zhao et al. have found that  $\text{Li}_2\text{SiO}_3$ -coated layered oxide  $\text{LiMO}_2$  cathodes delivered a relatively high discharge capacity compared to the pristine [35]. As a surface coating agent, the main roles of  $\text{Li}_2\text{SiO}_3$  have been considered as follows: (1) keeping the surface structural stability of cathode materials [34]; (2) suppressing the occurrence of the side reactions as a chemically inert material [34]; (3) improving the  $\text{Li}^+$ -ion conductivity [36]; (4) providing more  $\text{Li}^+$  ions during intercalation/deintercalation processes to improve the capacity [35]. For example, the coating of 1.5 wt%  $\text{Li}_2\text{SiO}_3$  lead to the increase in the discharge capacity of  $\text{Li}_{1.8}[\text{Mn}_{0.7}\text{Co}_{0.15}\text{Ni}_{0.15}]\text{O}_{2.675}$  from  $\sim 240$  to  $250 \text{ mAh g}^{-1}$  (increased by 4.17%) [34], while a 5 mol%  $\text{Li}_2\text{SiO}_3$  coated  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  electrode exhibited a discharge capacity of  $164.2 \text{ mAh g}^{-1}$  (increased by 6.27%) [37]. Therefore, it can be seen that the amorphous  $\text{Li}_2\text{SiO}_3$  coating layer has an important influence on the electrochemical performance. In addition, it may be inferred that the  $\text{Li}_2\text{SiO}_3$  may be used as a bridging agent to enhance electrochemical performance because of its excellent  $\text{Li}^+$ -ion conductivity [35]. Therefore, in this work, we used  $\text{Li}_2\text{SiO}_3$  as the modifying agent to improve the electrochemical performance of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  spinel cathode materials. As shown in Figs. 1a and b,  $\text{Li}_2\text{SiO}_3$  possesses a layer structure and exhibits three-dimensional (3-D) channels for  $\text{Li}^+$ -ion diffusion [36]. In the crystalline structure of  $\text{Li}_2\text{SiO}_3$ , the  $\text{SiO}_4$  tetrahedrons are tightly connected together by lithium ions [38].  $\text{Li}^+$  ions can transfer to each other via the (010) and (001) planes through 3-D channels for  $\text{Li}^+$ -ion diffusion [36]. On the other hand, Fig. 1c shows that a spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  also possesses the 3-D tunnels for fast  $\text{Li}^+$  ion transportation. It has been frequently reported that layer-structured cathodes can be well composited to spinel cathode materials, such as,  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2\text{-LiMn}_{1.5}\text{Ti}_{0.5}\text{O}_4$  [39],

$\text{Li}_2\text{MnO}_3\text{-Li}(\text{Mn}_{0.5}\text{Ni}_{0.5})\text{O}_2\text{-Li}[\text{Mn}_{1.5}\text{Ni}_{0.5}]\text{O}_4$  [40] and  $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2\text{-Li}[\text{Mn}_{1.5}\text{Ni}_{0.5}]\text{O}_4$  [41]. Because spinel (111) and layered (200) planes have similar close-packed planes [40,42,43], it may be inferred that the layer-structured  $\text{Li}_2\text{SiO}_3$  can be composited with the spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . In addition,  $\text{Li}_2\text{SiO}_3$  possesses a layer structure and exhibits three-dimensional (3-D) channels for  $\text{Li}^+$ -ion diffusion [36], while the spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  also possesses the 3-D tunnels for fast  $\text{Li}^+$  ion transportation. It can be reasonably anticipated that this compositing of  $\text{Li}_2\text{SiO}_3$  with  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  may lead to the synergy effect of the 3-D lithium ion channels between  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and  $\text{Li}_2\text{SiO}_3$ . The schematic view of the given composite materials is shown in Fig. 1d. It can be seen that the layer-structured  $\text{Li}_2\text{SiO}_3$  may act as bridging and/or coating agents in the composite materials. As a result, the compositing of layer-structured  $\text{Li}_2\text{SiO}_3$  with the spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  may present a new approach to enhance the electrochemical performance of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ -based materials. In this work, novel (1-x)  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4\cdot x\text{Li}_2\text{SiO}_3$  cathode composites have been developed and synthesized via a citric acid-assisted sol-gel method; and the phase structure, micromorphology and electrochemical performance of the pristine and modified samples have been systematically investigated. The obtained cathode composites exhibit the significant enhancement in the capacity and rate capability for high-performance and high-voltage lithium-ion batteries.

## 2. Experimental

### 2.1. Synthesis of the (1-x) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4\cdot x\text{Li}_2\text{SiO}_3$ composites

(1-x) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4\cdot x\text{Li}_2\text{SiO}_3$  (LNM-LS-x, x = 0, 0.05, 0.1, 0.15, 0.2 and 0.3) nominal composites were synthesized by a citric acid-assisted sol-gel method. Stoichiometric amounts of lithium acetate ( $\text{LiAc}\cdot 2\text{H}_2\text{O}$ , 99.0%, Sinopharm), manganese acetate ( $\text{Mn}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$ , 99%, Sinopharm) and nickel acetate ( $\text{Ni}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$ , 98.0%, Sinopharm) were dissolved in deionized water. After



**Fig. 1.** The crystalline structure of  $\text{Li}_2\text{SiO}_3$ : (a) the (010) plane, (b) the (001) plane; (c) the crystalline structure of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ; and (d) the schematic view of the given composite materials (LNM –  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ; LS –  $\text{Li}_2\text{SiO}_3$ ).

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