



# High performance $\text{Li}_2\text{MnSiO}_4$ prepared in molten $\text{KCl-NaCl}$ for rechargeable lithium ion batteries



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## ABSTRACT

$\text{Li}_2\text{MnSiO}_4/\text{C}$  composites have been prepared by a facile molten salt method followed by a carbon coating process. Submicron  $\text{Li}_2\text{MnSiO}_4$  particles are obtained in  $\text{KCl-NaCl}$  molten phase with a short reaction time of 3 h. The orthorhombic structure and sphere-like morphology are confirmed by X-ray diffraction and scanning electron microscope. Ex-situ XRD study confirms amorphous transition of  $\text{Li}_2\text{MnSiO}_4$  during the first charge process. Galvanostatic charge-discharge tests display high initial charge and discharge capacities of 265 and 194  $\text{mAh g}^{-1}$ , respectively, at 0.05 C rate for the  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composite prepared at 700 °C. At 0.1 C rate, it maintains a discharge capacity of 165  $\text{mAh g}^{-1}$  and its capacity retention at the 50<sup>th</sup> cycle is up to 78%, showing superior cycling stability.

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## 1. Introduction

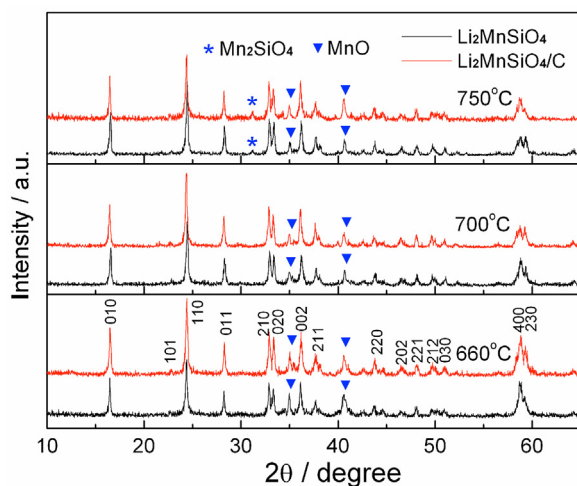
Great attention has been paid to next-generation safe lithium batteries with high energy and power densities for vehicle applications and energy storage. The low practical capacity and safety issue of currently commercialized lithium transition metal oxides cathode materials, such as  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , etc., can not meet the demand of high performance battery systems [1,2]. Lithium orthosilicates,  $\text{Li}_2\text{MSiO}_4$  (M = Fe, Mn and Co), have recently attracted tremendous interests on account of their high theoretical capacities ( $>330 \text{ mAh g}^{-1}$ ) corresponding to a two electron ( $2 \text{ Li}^+$ ) reaction and good thermal stability from strong Si-O bonding [3–6]. Due to the possible oxidation of the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  couple rather than  $\text{Fe}^{3+}/\text{Fe}^{4+}$  and  $\text{Co}^{3+}/\text{Co}^{4+}$  couples within the potential range of present electrolyte systems, the insertion/extraction of two  $\text{Li}^+$  ions is much more feasible in  $\text{Li}_2\text{MnSiO}_4$  than that in  $\text{Li}_2\text{FeSiO}_4$  and  $\text{Li}_2\text{CoSiO}_4$  [7–9]. However,  $\text{Li}_2\text{MnSiO}_4$  has two main shortcomings, low electronic conductivity ( $\sim 10^{-16} \text{ S cm}^{-1}$ ) and slow kinetics, which would result in a poor electrochemical activity [10,11].

Similar to  $\text{LiFePO}_4$  material, several approaches including surface carbon coating, metal ion doping and nanoparticles preparation have been pursued to achieve the high capacity of  $\text{Li}_2\text{MnSiO}_4$  [12–15]. Recently, the nano-sized  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composites with the

particle size less than 50 nm were successfully synthesized by solution route [16], solvothermal method [17], sol-gel route [18–20] and microwave-solvothermal process [21,22]. The initial discharge capacities of the composites were beyond  $200 \text{ mAh g}^{-1}$ , while the capacity dropped dramatically after several cycles and its capacity retention was less than 50% after 20 cycles. The fast capacity fade may be ascribed to the conversion from crystal structure to amorphous phase during the electrochemical cycling [16,19,22]. More recently, Liu et al. [23] reported a solid-state reaction for carbon coated  $\text{Li}_2\text{MnSiO}_4$  nanoparticles using citric acid as the carbon source. At the rate of 0.05 C, the  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composites delivered an initial discharge capacity of 268  $\text{mAh g}^{-1}$  and showed a reversible capacity of 136  $\text{mAh g}^{-1}$  up to 140 cycles. Zhao et al. [24] synthesized a carbon coated  $\text{Li}_2\text{MnSiO}_4$  composite, which was uniformly distributed on reduced graphene oxide (RGO) networks. The  $\text{RGO@Li}_2\text{MnSiO}_4/\text{C}$  composite presented excellent cyclability with a stable capacity of 150  $\text{mAh g}^{-1}$  for 700 cycles at 1 C. The above results indicate that the cycling performance of  $\text{Li}_2\text{MnSiO}_4/\text{C}$  is strongly affected by the preparation process and the microstructural perfection of the material. The molten salt method has been widely employed to prepare multi-component oxides powders with controllable particle morphology and excellent electrochemical performance [25,26]. Molten salts as a reaction media could provide a liquid reaction environment for reactants, thereby accelerating the reaction rate and providing a homogeneous structure of the final product [27]. However, to the best of our knowledge, the molten salt synthesis of  $\text{Li}_2\text{MnSiO}_4$  has rarely been studied so far.

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**Fig. 1.** XRD patterns of  $\text{Li}_2\text{MnSiO}_4$  and  $\text{Li}_2\text{MnSiO}_4/\text{C}$  prepared at various temperatures.

In this work, well-dispersed  $\text{Li}_2\text{MnSiO}_4$  particles have been synthesized by a facile molten salt method using the mixture of KCl and NaCl as the reaction medium. To enhance the surface electronic conductivity, sucrose and acetylene black are adopted as carbon sources to coat the  $\text{Li}_2\text{MnSiO}_4$  particles with a thin carbon layer. The effects of the material structure and morphology on the electrochemical performances of  $\text{Li}_2\text{MnSiO}_4/\text{C}$  are discussed and compared.

## 2. Experimental

### 2.1. Sample Synthesis

$\text{Li}_2\text{MnSiO}_4$  particles were prepared by a molten salt method. An equal molar ratio of KCl and NaCl with a melting point of 658 °C acts as flux after drying at 100 °C for 2 h under vacuum.  $\text{Li}_2\text{CO}_3$ ,  $\text{MnCO}_3$ ,  $\text{SiO}_2$  (10–20 nm) and KCl–NaCl in a molar ratio of 1:1:1:4 were well mixed with a mortar and pestle. Then, the mixed powders were

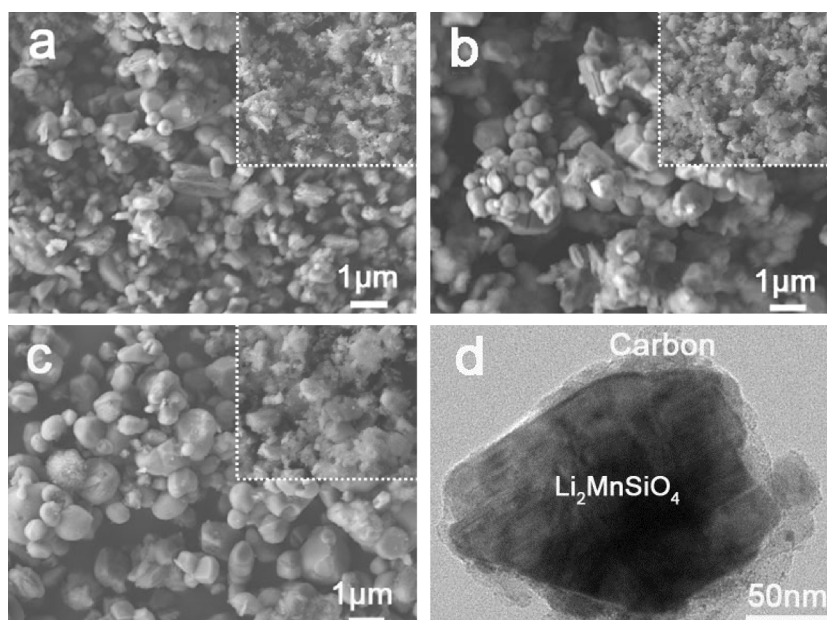
transferred to a tube furnace and heated at 350 °C for 2 h, followed by treatment at different temperatures (660, 700 and 750 °C) for 3 h in  $\text{H}_2/\text{Ar}$  (5 vol%) atmosphere. Finally, the product was washed with deionized water to dissolve any remaining salt, filtered and dried in vacuum. The obtained  $\text{Li}_2\text{MnSiO}_4$  powder was mixed with a certain amount of sucrose and acetylene black, and then calcined at 600 °C in Ar atmosphere for 2 h to obtain  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composites.

### 2.2. Sample analysis

Powder X-ray diffraction (XRD) patterns of the prepared  $\text{Li}_2\text{MnSiO}_4$  were recorded on a Rigaku D/Max-2200 diffractometer using Cu  $\text{K}\alpha$  radiation (40 kV, 30 mA). The morphologies of the  $\text{Li}_2\text{MnSiO}_4$  and  $\text{Li}_2\text{MnSiO}_4/\text{C}$  samples were observed by a field emission scanning electron microscope (FESEM, JEOL JSM-7401F) with an accelerating voltage of 5.0 kV and a high resolution transmission electron microscope (HRTEM, JEOL JEM-2100) operating at 200 kV. The carbon content of the  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composites was measured with PE 2400II elemental analyzer.

### 2.3. Electrochemical Measurements

Electrochemical measurements were performed using CR2016 coin-type cells with Celgard 2400 membrane as separator and metallic lithium foil as anode. The cathode was composed of 85 wt%  $\text{Li}_2\text{MnSiO}_4/\text{C}$ , 5 wt% Super P conductive carbon and 10 wt% polyvinylidene difluoride (PVDF). 1 M  $\text{LiPF}_6$  in 50:50 (v/v) ethylene carbonate (EC)/dimethyl carbonate (DMC) was used as the electrolyte. Galvanostatic charge/discharge cycling was carried out on a Land battery testing system (CT2001, Wuhan, China) in a potential range of 1.5–5.0 V at room temperature. Cyclic voltammetry (CV) was performed on an electrochemical workstation (CHI660D, Shanghai, China). Electrochemical impedance spectroscopic measurement (EIS) was conducted on a Solartron SI1287 electrochemical interface in the frequency range of 100 kHz to 10 mHz. The specific capacity was calculated based on the mass of pure orthosilicate active material.



**Fig. 2.** SEM images of  $\text{Li}_2\text{MnSiO}_4$  and  $\text{Li}_2\text{MnSiO}_4/\text{C}$  (inset) prepared at 660 °C (a), 700 °C (b) and 750 °C (c); TEM image of the  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composite (d).

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